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# CHEMISTRY

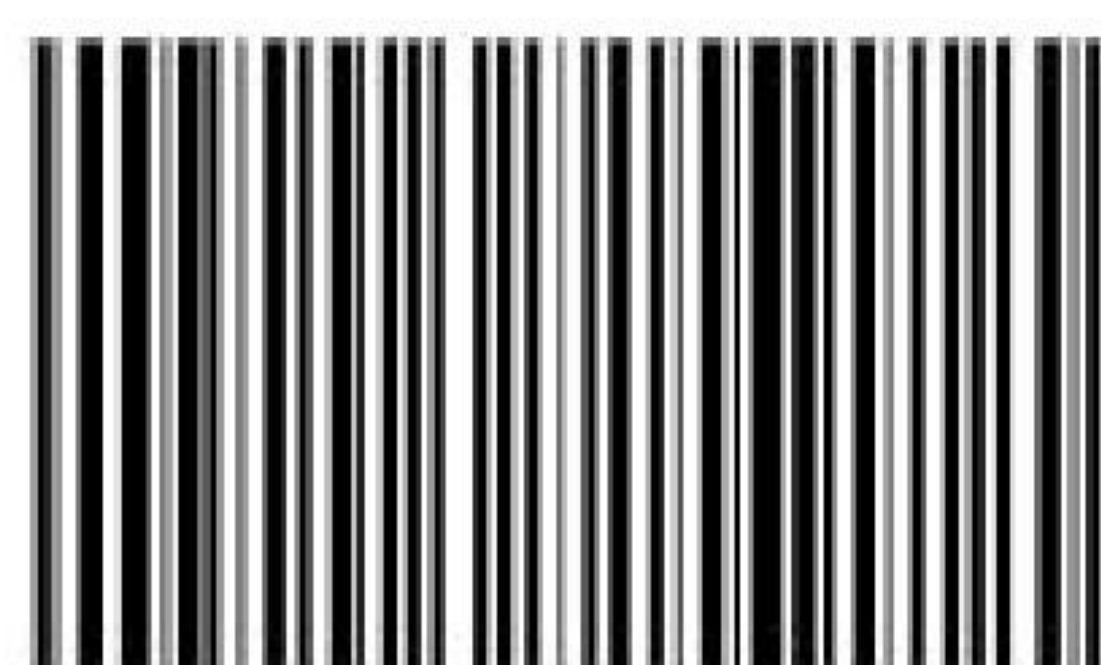
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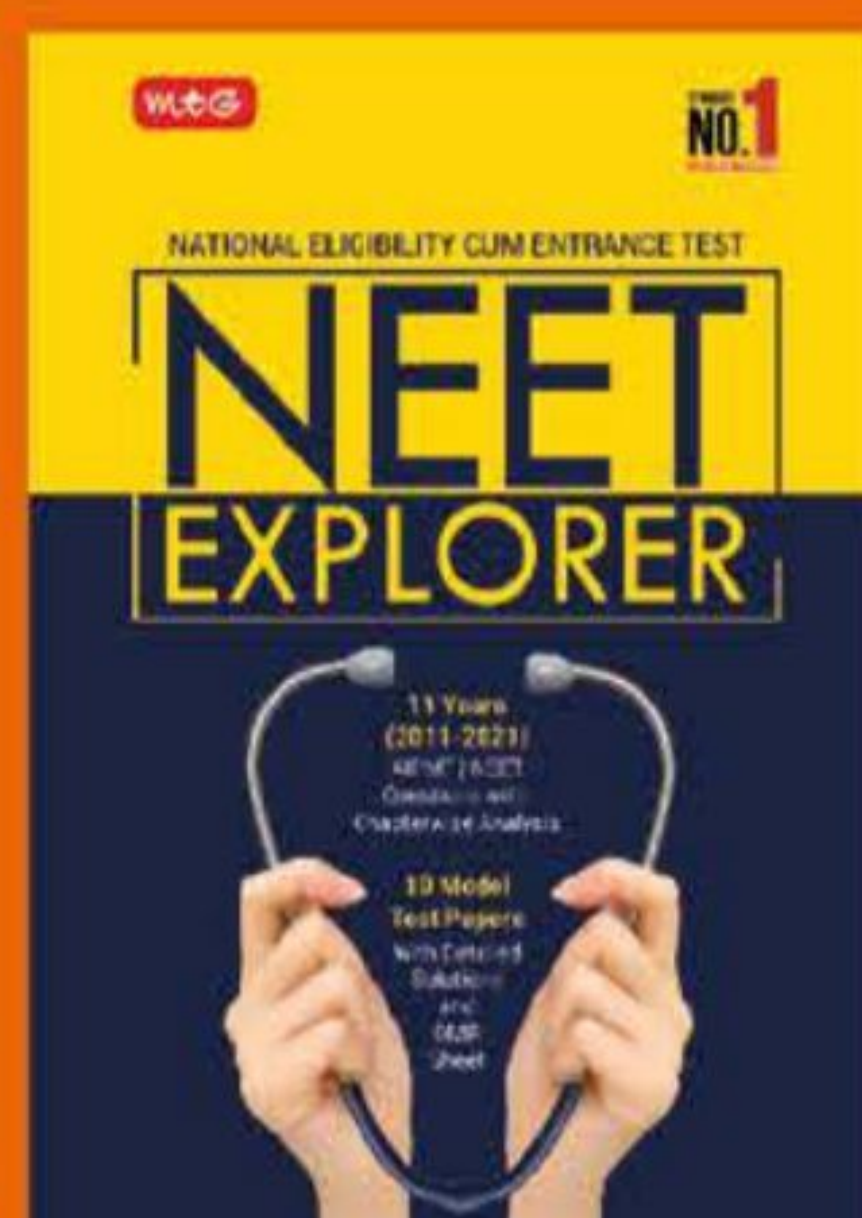
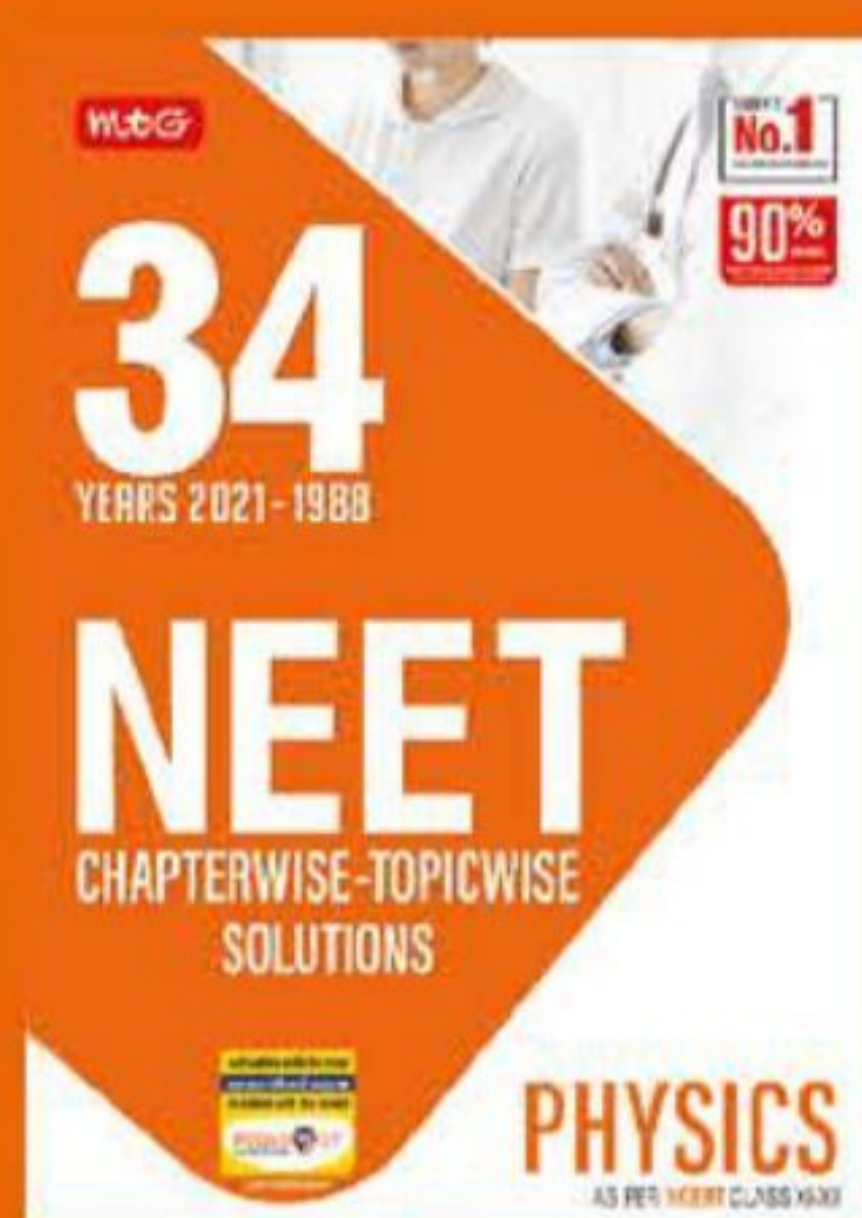
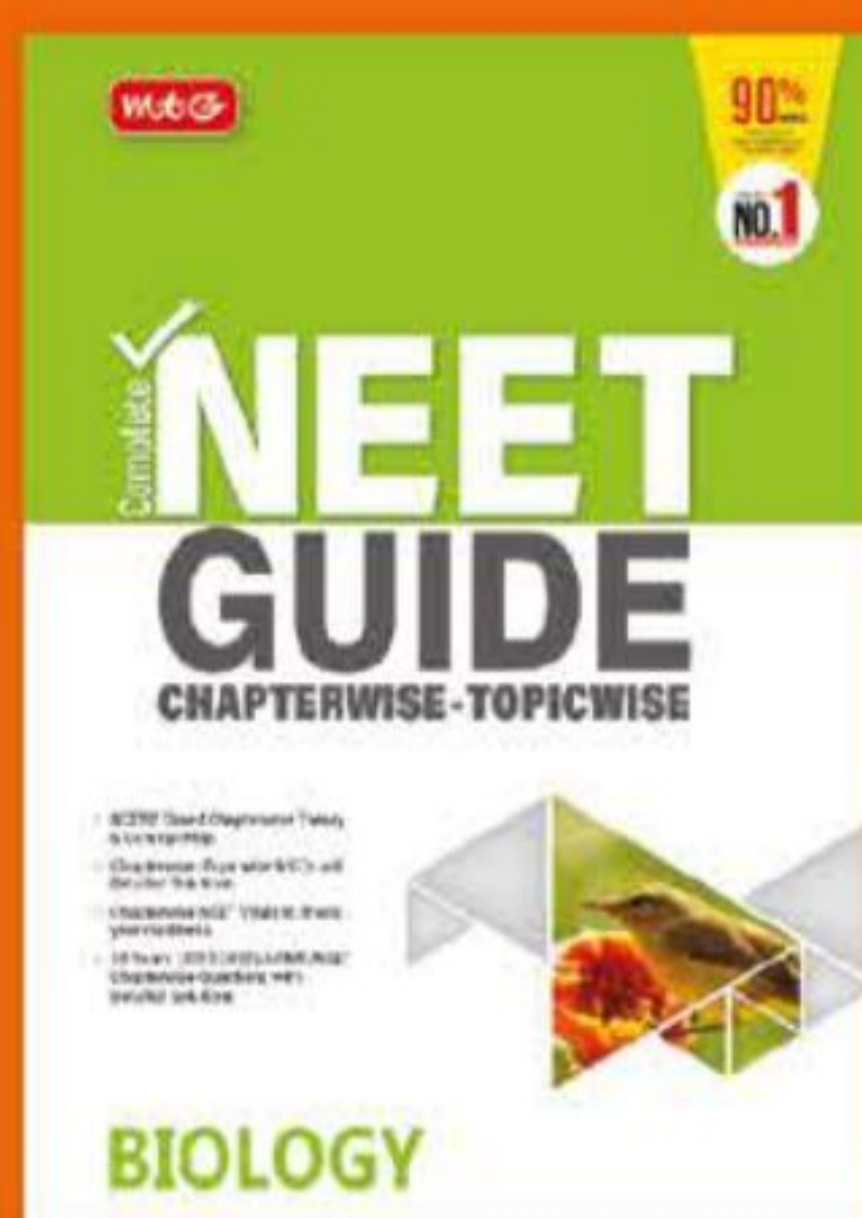
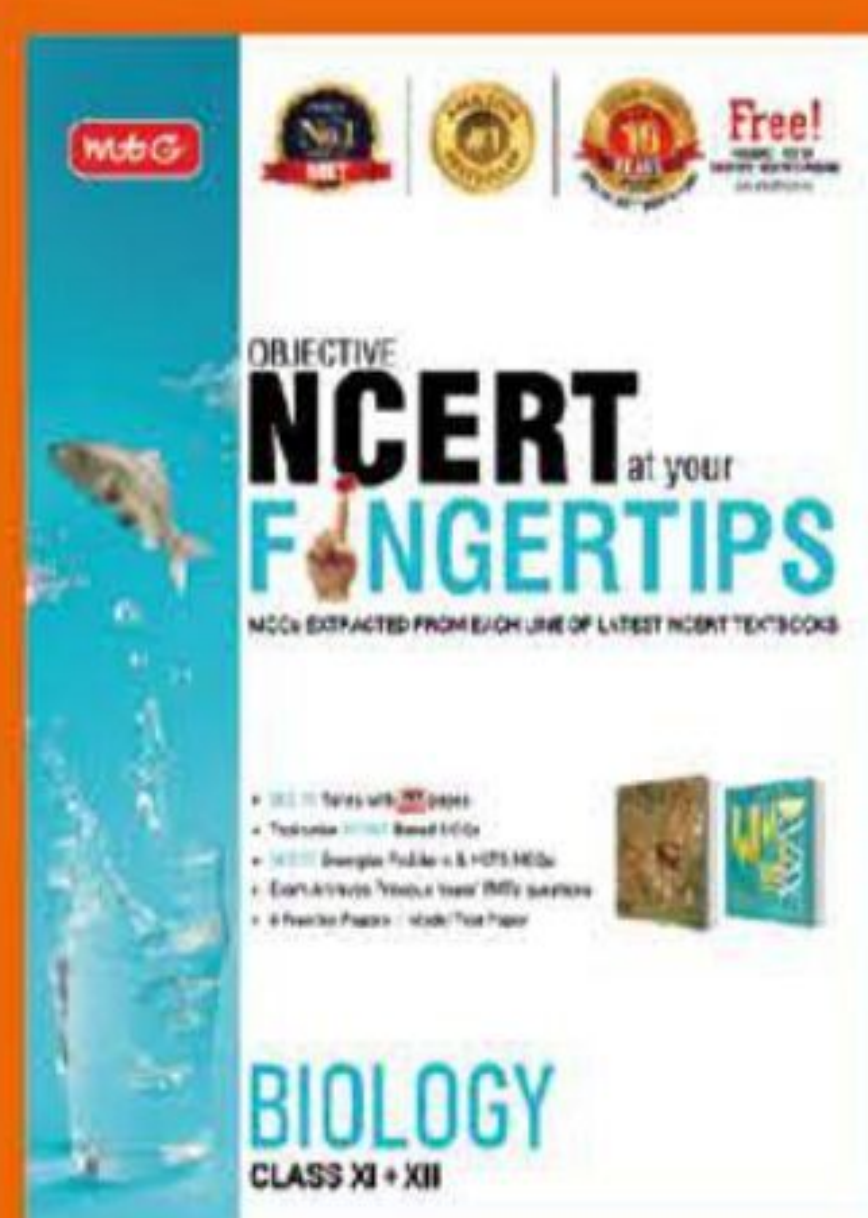
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# Tips on Revision

*Preparing for JEE and NEET is a lot of work. But you know that already. Did you know revision can be a little less work if you plan right? Find out how.*

Our memory requires a bit of a refresher every once in a while. Be it a favourite novel, a place or academics. Especially academics, and more so if you are appearing for JEE or NEET. So, all those students dreaming of donning the scrubs should know that revision is an important and integral part of preparing for JEE and NEET.

You must know that along with efficient preparation, strategic revision is equally important. Here are some tips for JEE and NEET revision:

## 1. Make a Proper Schedule

Plan ahead, chalk out a proper schedule for revision. Allot sufficient time to each topic and subject based on the time you have left before the exam. A good idea is to start with topics that you find tough so that you can devote more time to them. An ideal way to ensure that you do this is by preparing a list of topics segregated into three categories: Need a lot of work, Need some work, Need to flip through. You can then designate the number of days/hours that each of these topics need and take it from there.

## 2. Go through the syllabus, exam pattern

Keep tab on the exam pattern and syllabus so that you can prepare accordingly. This is crucial because the syllabus or pattern might have changed since you started preparation! So be alert and double check.

## 3. Clear basic concepts of numerical-related topics

While NEET is not as concept-oriented as some other undergraduate exams, and JEE is more concept oriented. Physics and Chemistry still rely heavily on conceptual grasp of all topics. Numerical-based questions in these subjects, especially Physics, can be solved easily if your concepts are clear. You can score well in JEE and NEET with an above average understanding of basic concepts.

## 4. Compile all revision resources

You would need NCERT books of Physics, Chemistry, Math and Biology ready, as well as previous year question papers and notes that you have prepared earlier. Form a habit of marking important or difficult questions. This will come handy while revising.

## 5. Take Mock Tests

Taking mock tests is the best way to understand your last-minute preparation level. Solving questions of different difficulty

levels along with previous year papers, mock tests, and practice sheets should form an integral part of your daily revision routine. Taking tests regularly also reduces the time it usually takes you to answer a question. This in turn will improve your score in the time-bound JEE and NEET examination.

## 6. Do not prioritise favourites

Every student has his or her favourite subject/s. It's easy to study those over other tougher ones. However, for a competitive exam like JEE or NEET, all the subjects need to be studied with equal dedication. A way out of this is to devise a timetable in such a way that you alternate between your favourite subjects with the ones you find difficult while revising.

## 7. Do not take up new topics

You need to know how to utilise your time just before the exam. There are chances that you may have missed studying certain topics. Now is not the time to pick those up. Taking up a new topic will only be a waste of time. Be smart. Focus on strengthening the topics that you are well-versed with.

## 8. Prepare a formula sheet

For Physics and Chemistry, a pre-prepared formula sheet goes a long way in easy revision. Use it. It helps avoid glitches during the examination. Add new formulas to your sheet as and when you study a topic, instead of spending a huge amount of time in the end on just preparing the formula sheet. This will help you memorise and retain your study material better.

## 9. Limit distractions

Distractions happen when fatigue sets in. Try to limit those including scrolling aimlessly on social media websites. They tend to be addictive. Instead, catch an episode of your favourite series, or go for a walk when you feel mentally exhausted.

Studying non-stop is known to hinder performance. Take short breaks. These help you relax your mind, improve concentration and retention. A calm mind is better than a tired one. We hope you can incorporate some or all of the tips to help you revise better, smarter.

All the best!

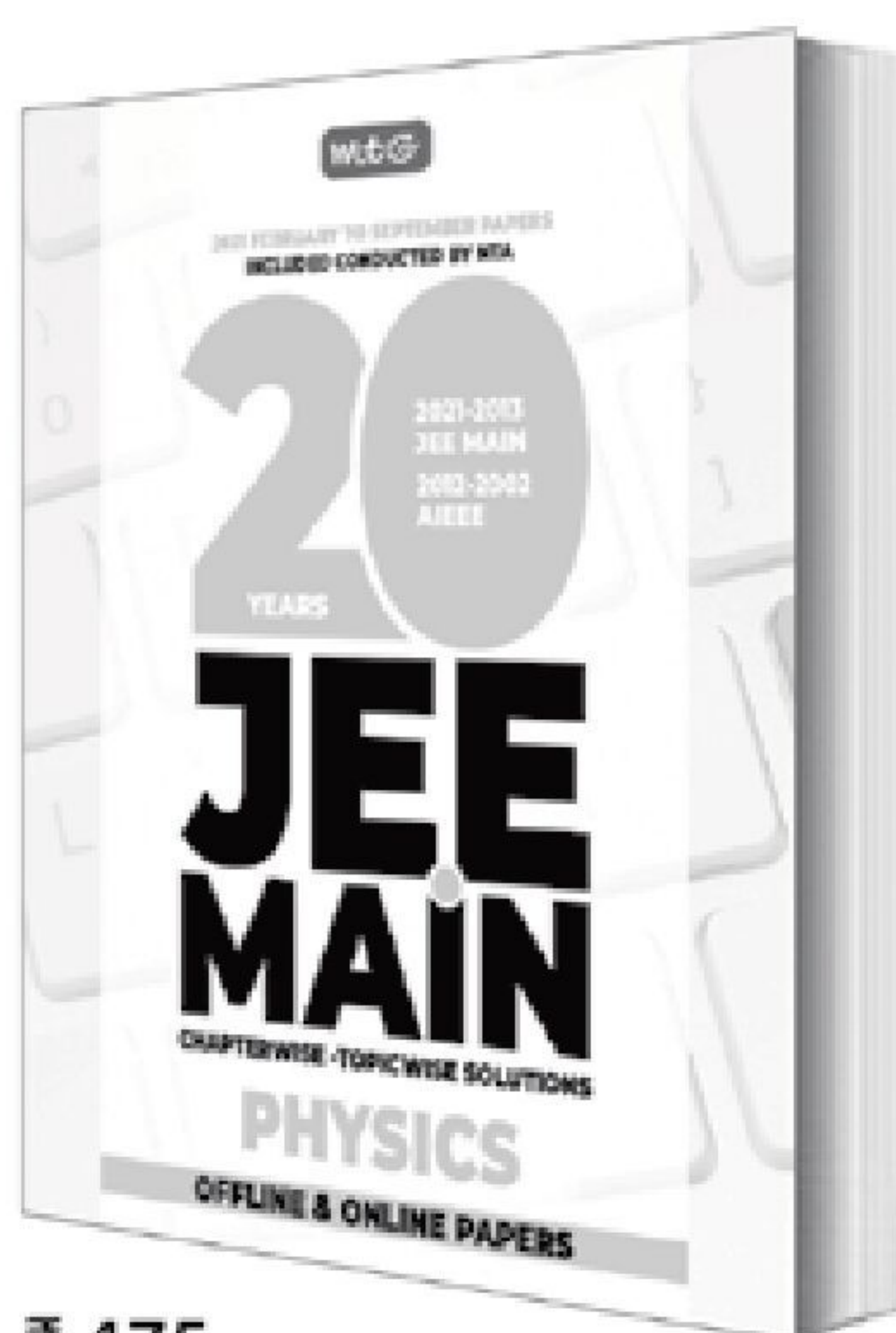
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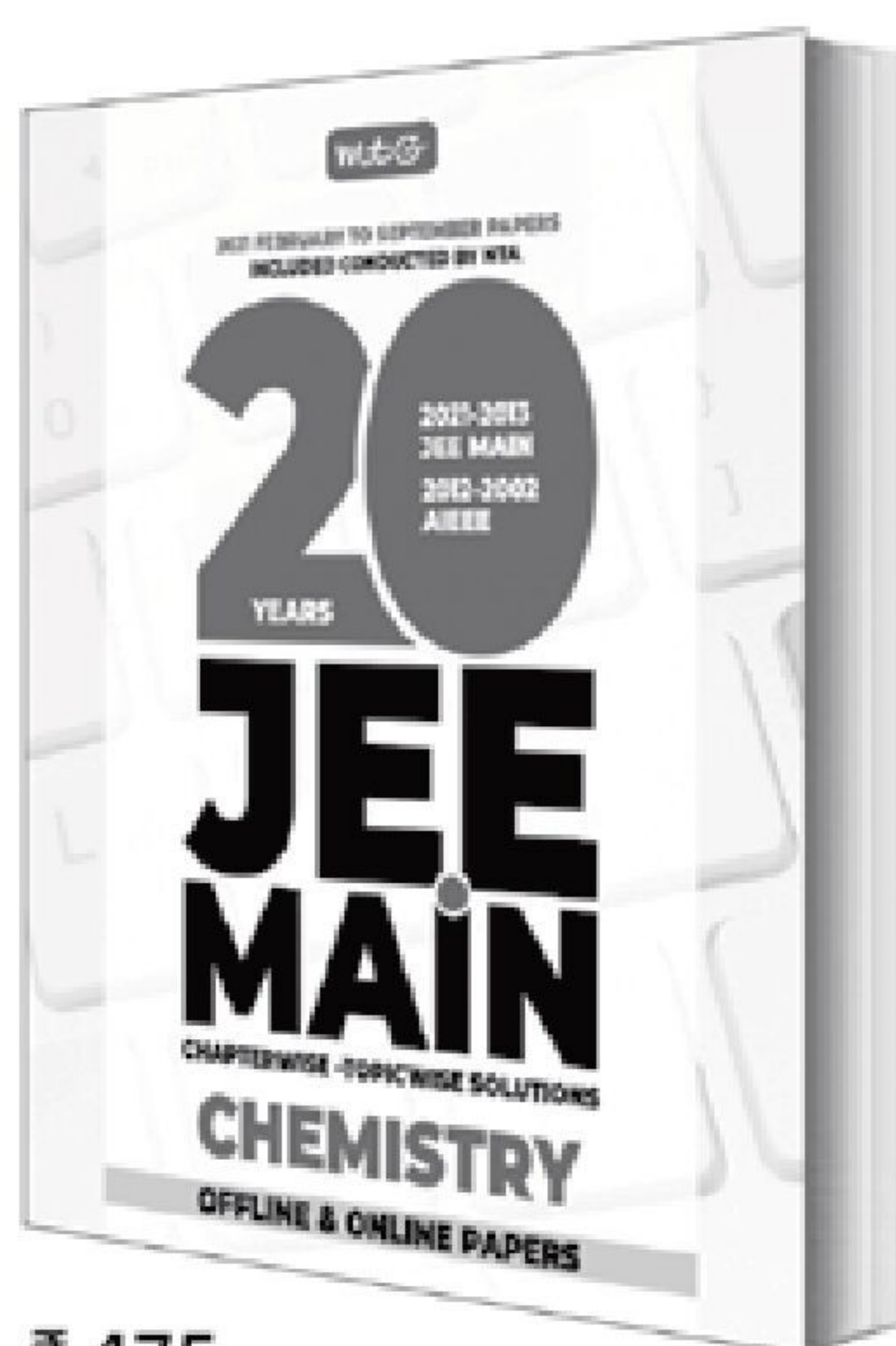


# The Best tool for success in JEE Main

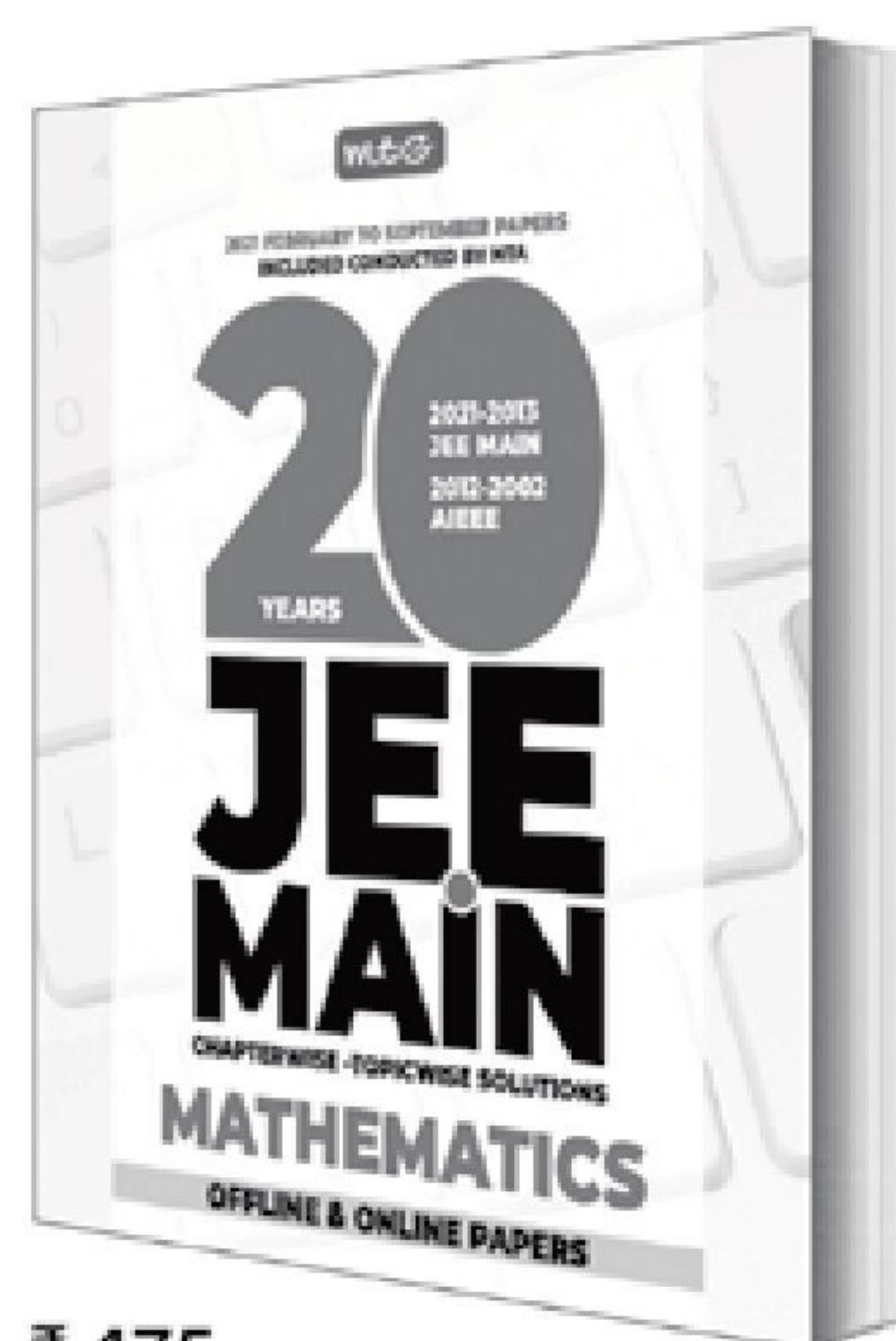
20 Years' JEE Main Chapterwise-Topicwise Solutions Physics, Chemistry and Mathematics contain not only chapterwise - topicwise questions that have appeared over the last 20 years in JEE Main / AIEEE but also their complete solutions. Needless to say these books are essential for any student to compete successfully in JEE Main.



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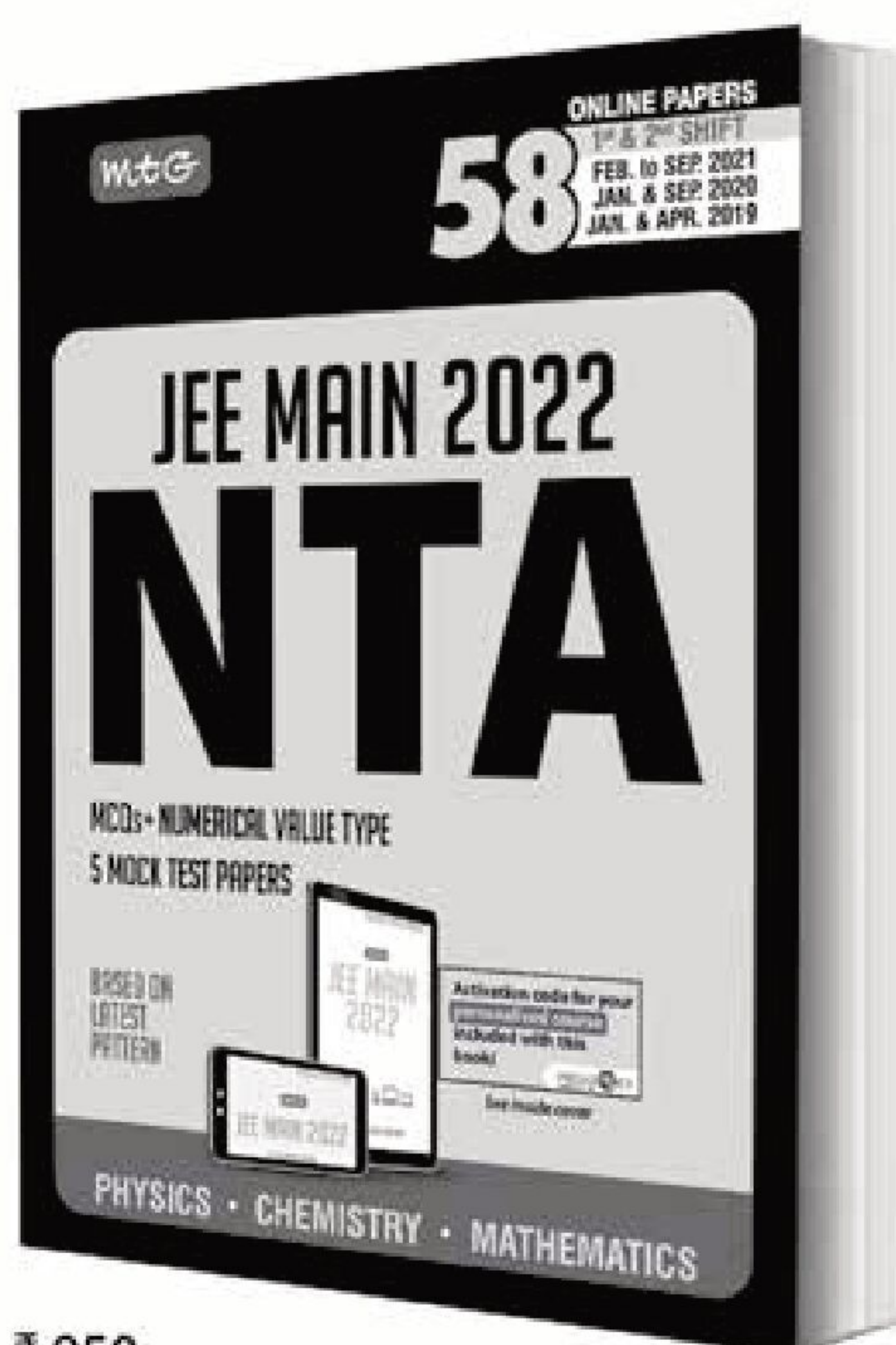
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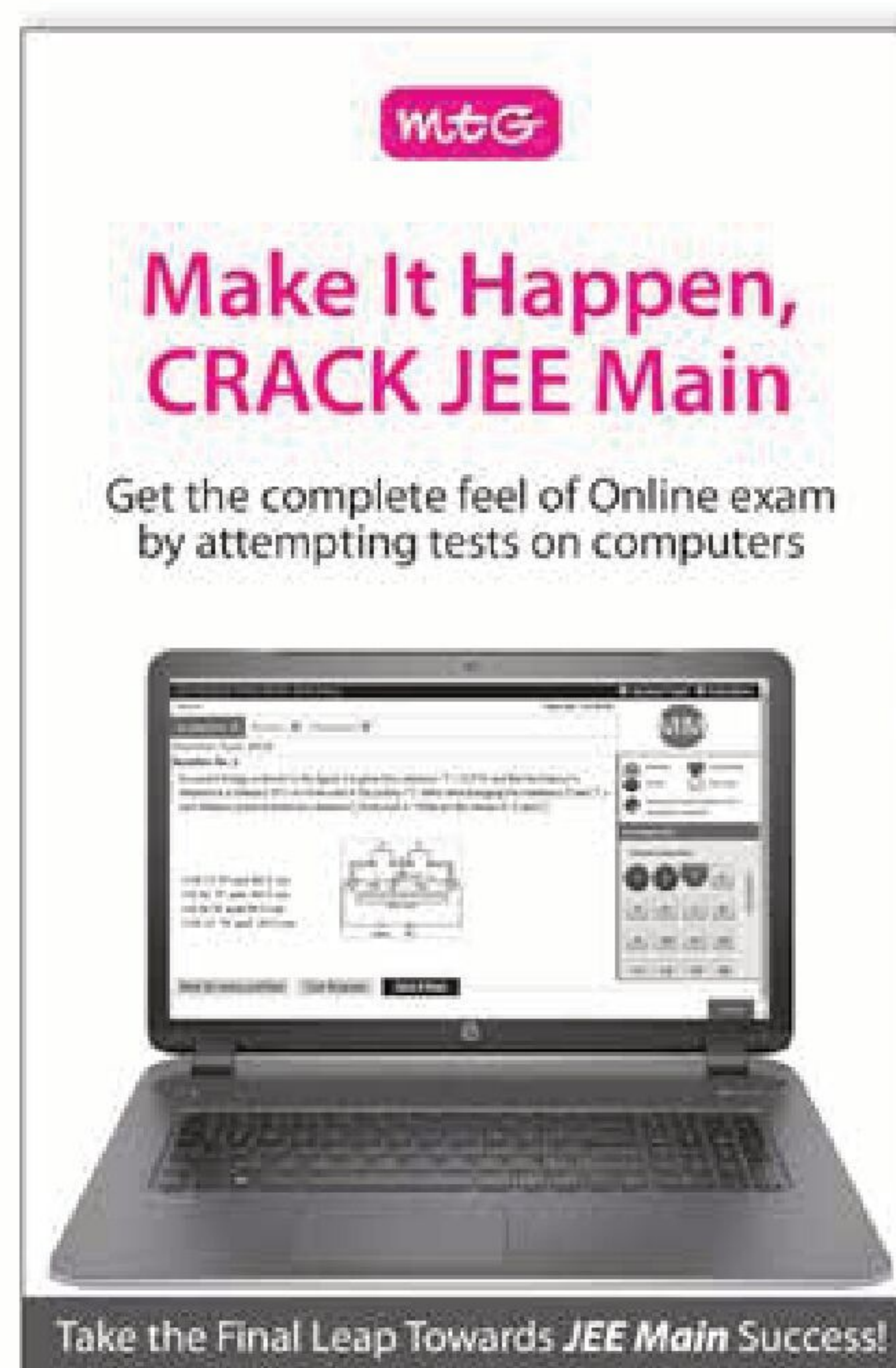
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## Highlights

- Fully Solved Authentic Papers
- 26 (Feb, March, July & Sept. 2021) + 16 (Jan. & Sept., 2020) + 16 (Jan. & Apr., 2019) Online Papers
- 4915 MCQs for Practice
- Chapterwise Tabular and Graphical Analysis Showing the Weightage of Chapters
- 5 MTPs as per the latest JEE Main pattern

Practice Online Tests to Predict Your Rank

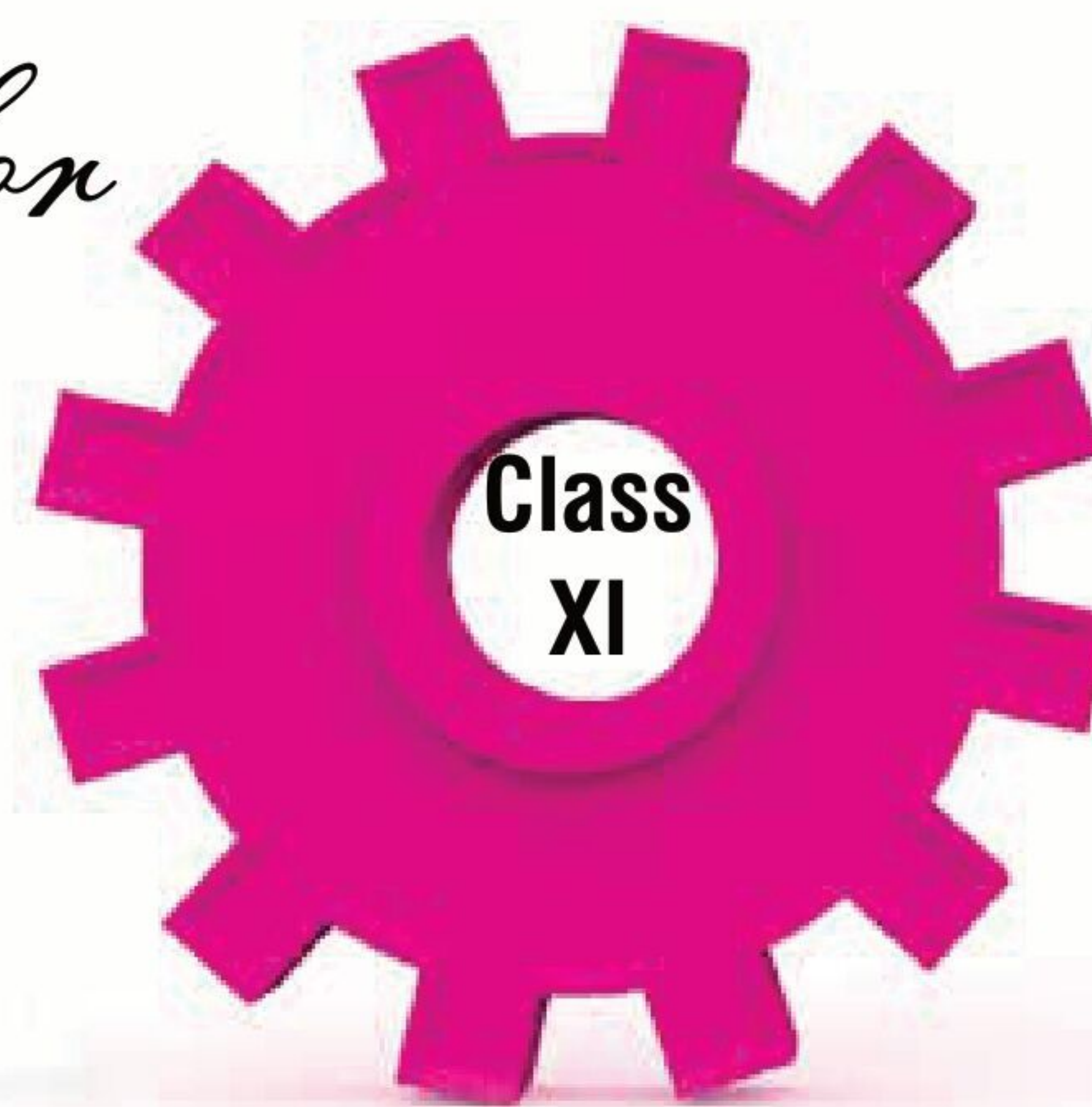
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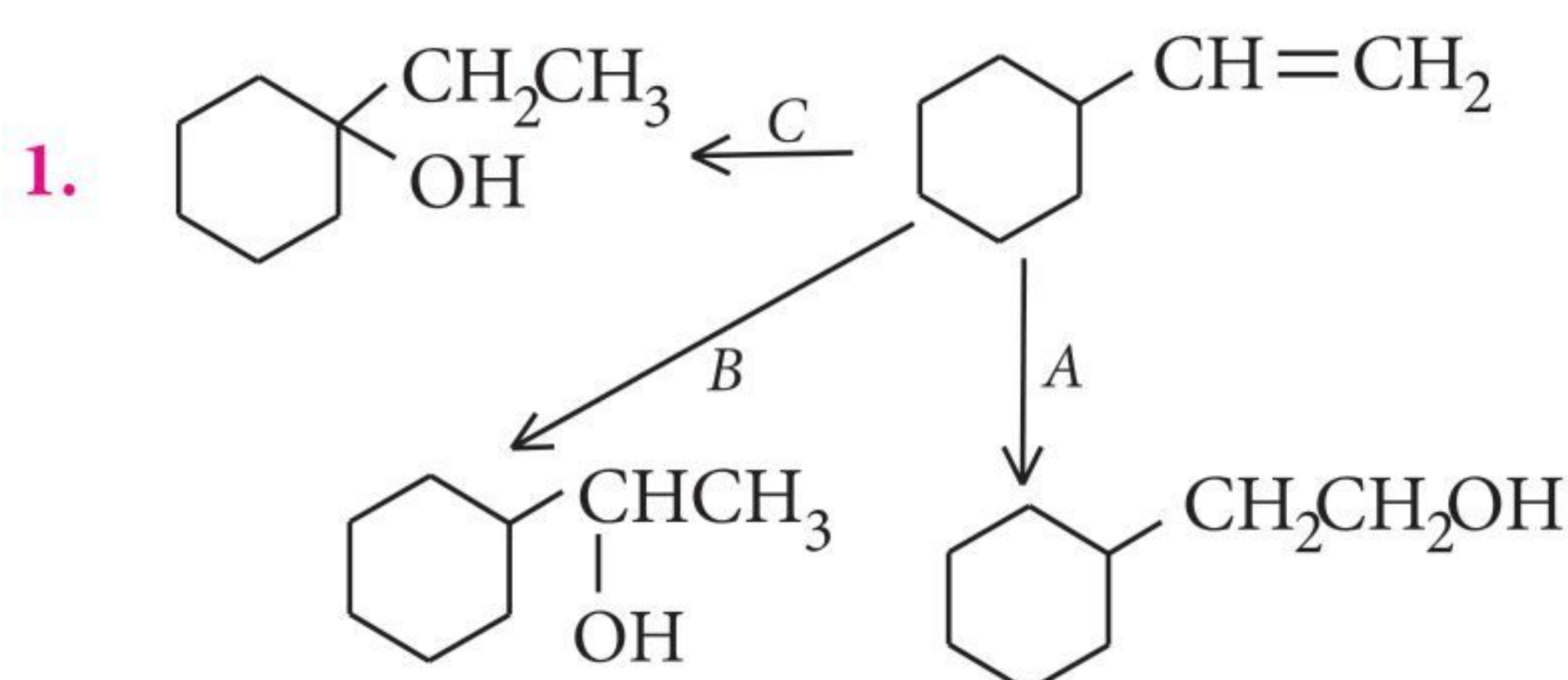


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with exclusive and brain storming MCQs

Practicing these MCQs help to strengthen your concepts and give you extra edge in your JEE preparation

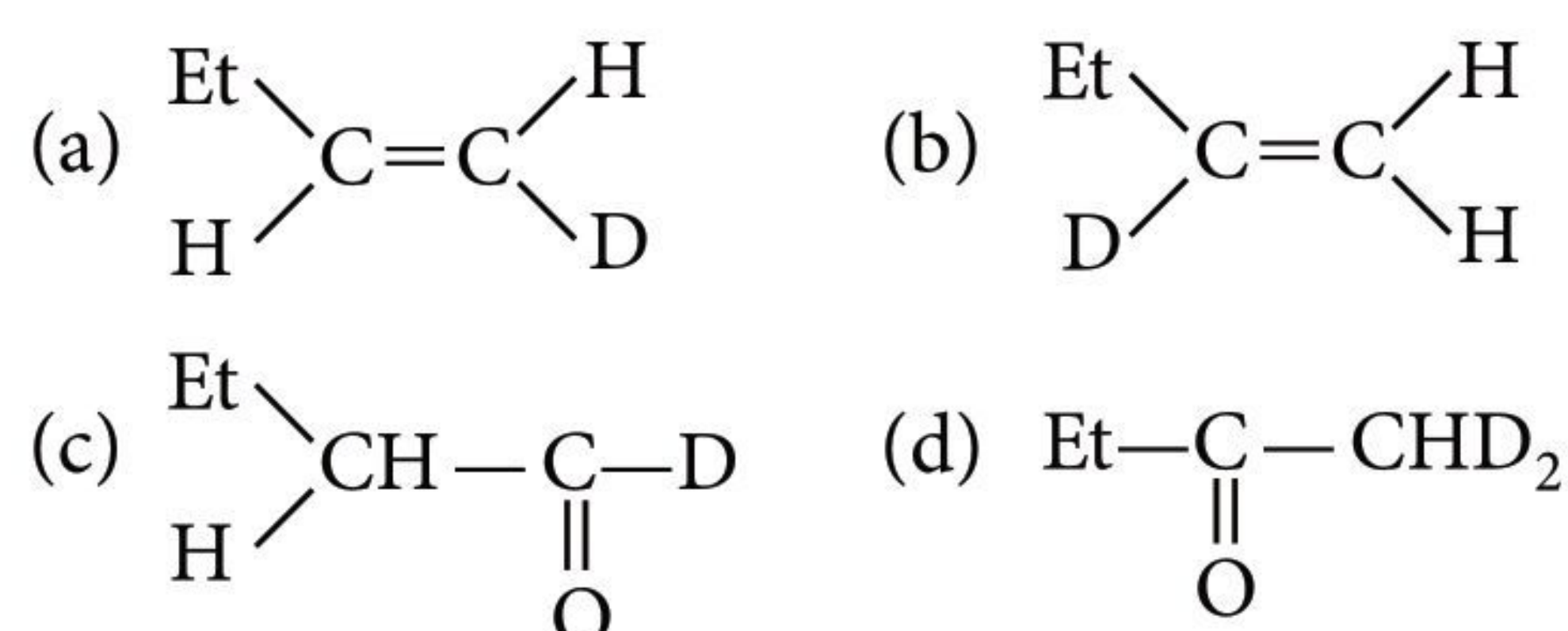


Schemes A, B, C are respectively

- I. acid-catalysed hydration
- II. hydroboration-oxidation
- III. oxymercuration-demercuration
- (a) I in all cases                      (b) I, II, III
- (c) II, III, I                              (d) III, I, II

2. The solutions A and B are 0.1 and 0.2 molar in concentration. If 100 mL of A are mixed with 25 mL of B and there is no change in volume, then the final molarity of the solution is
- (a) 0.15 M                              (b) 0.18 M
  - (c) 0.12 M                              (d) 0.30 M
3. Consider two elements with atomic no. 37 and 53, the bond between their atoms would be
- (a) covalent                              (b) ionic
  - (c) coordinate                              (d) metallic.

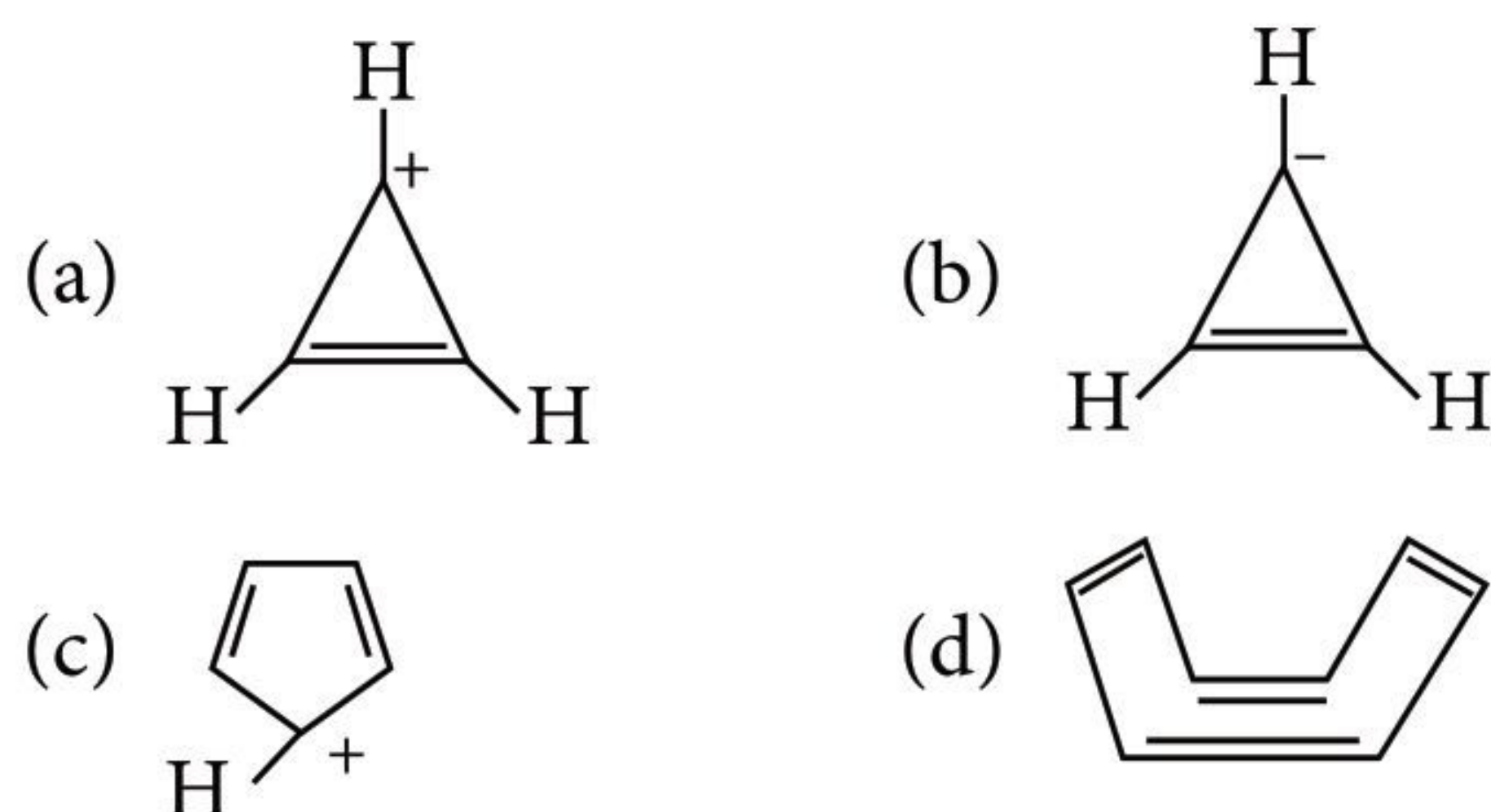
4. The major product 'P' in the following reaction is
- $$\text{CH}_3\text{CH}_2\text{C}\equiv\text{CH} \xrightarrow[\text{THF}]{\text{BD}_3} \xrightarrow{\text{CH}_3\text{COOH}} \text{P}$$



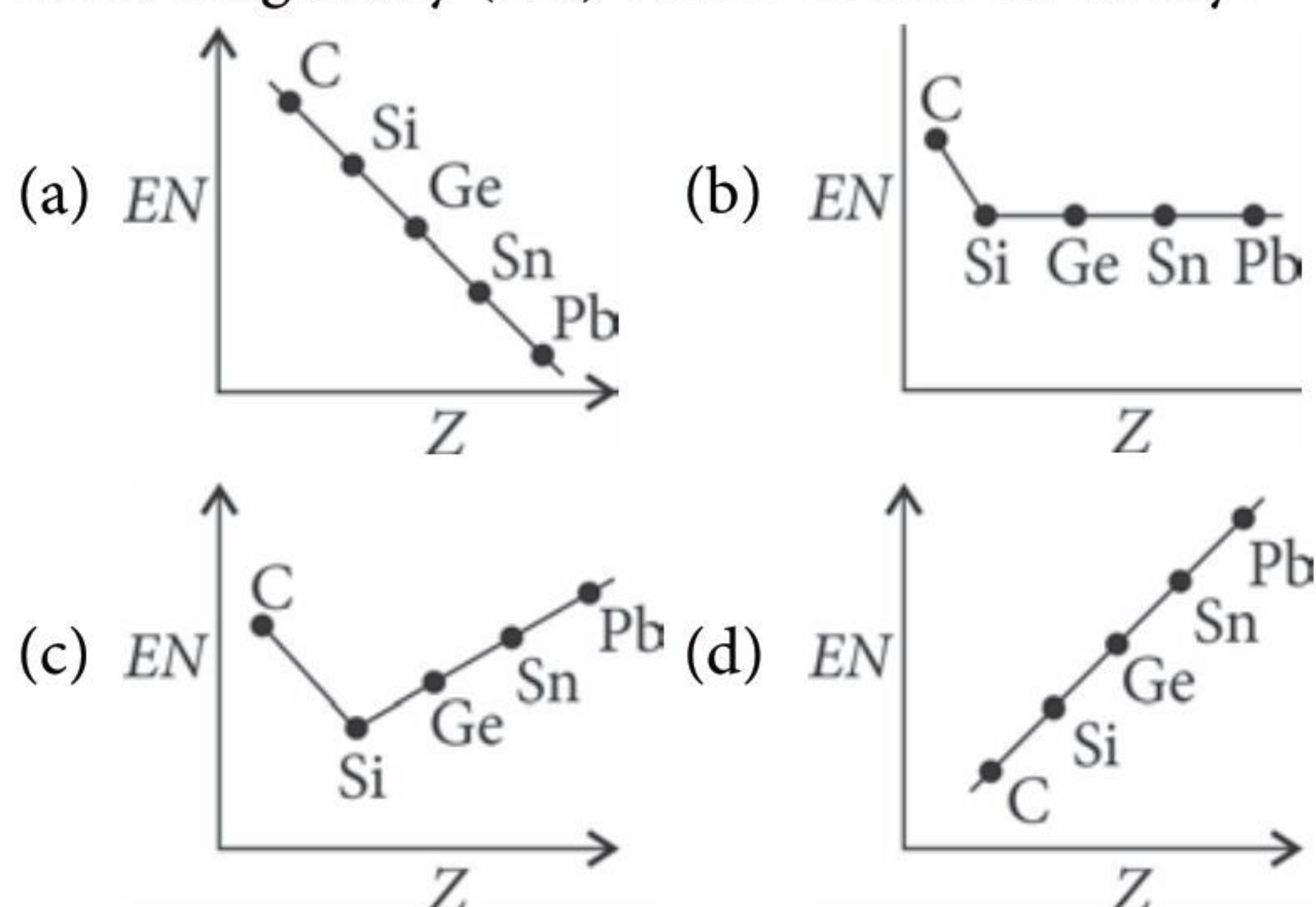
5. In winter season, special type of clouds called Polar Stratospheric Clouds (PSC) are formed over Antarctica. As a result, less depletion of ozone layer takes place due to reactions
- (a)  $\text{ClONO}_2 + \text{H}_2\text{O} \longrightarrow \text{HOCl} + \text{HNO}_3$
  - (b)  $\text{ClONO}_2 + \text{HCl} \longrightarrow \text{Cl}_2 + \text{HNO}_3$
  - (c) both (a) and (b)
  - (d) none of these.
6. The energy levels for  $A^{+(Z-1)}$  can be given by
- (a)  $E_n$  for  $A^{+(Z-1)} = Z^2 \times E_n$  for H
  - (b)  $E_n$  for  $A^{+(Z-1)} = Z \times E_n$  for H
  - (c)  $E_n$  for  $A^{+(Z-1)} = \frac{1}{Z^2} \times E_n$  for H
  - (d)  $E_n$  for  $A^{+(Z-1)} = \frac{1}{Z} \times E_n$  for H



7. The correct order of the increasing s-character of the orbital of B which overlaps with the orbital of F to form B—F bond in  $\text{BF}_2^+$ ,  $\text{BF}_3$  and  $\text{BF}_4^-$  is  
 (a)  $\text{BF}_2^+ < \text{BF}_4^- < \text{BF}_3$  (b)  $\text{BF}_3 < \text{BF}_2^+ < \text{BF}_4^-$   
 (c)  $\text{BF}_2^+ < \text{BF}_3 < \text{BF}_4^-$  (d)  $\text{BF}_4^- < \text{BF}_3 < \text{BF}_2^+$
8. Which of the following is an aromatic compound?



9.  $\text{Be}_2\text{C} + 4\text{H}_2\text{O} \longrightarrow 2\text{X} + \text{CH}_4$   
 $\text{X} + 2\text{HCl}_{(aq)} \longrightarrow \text{Y}$   
 X and Y formed in the above two reactions are  
 (a)  $\text{BeCO}_3$  and  $\text{Be}(\text{OH})_2$  respectively  
 (b)  $\text{Be}(\text{OH})_2$  and  $\text{BeCl}_2$  respectively  
 (c)  $\text{Be}(\text{OH})_2$  and  $[\text{Be}(\text{OH})_4]\text{Cl}_2$  respectively  
 (d)  $[\text{Be}(\text{OH})_4]^{2-}$  and  $\text{BeCl}_2$  respectively.
10. Which of the following is the correct graph for electronegativity (EN) values of carbon family?



### NUMERICAL PROBLEMS

11. Boiling point of a liquid is 50 K at 1 atm and  $\Delta H_{\text{vap}} = 460.6 \text{ cal mol}^{-1}$ . What will be its b.pt. (in K) at 10 atm?
12. 5.0 L water is placed in a closed room of volume  $2.5 \times 10^4 \text{ L}$  having temperature 300 K. If vapour pressure of water is 27.0 mm and density is  $0.990 \text{ g/cm}^3$  at this temperature, how much water (in mL) is left in liquid state?
13. For the given reaction :  
 $\text{IO}_3^- + a\text{I}^- + b\text{H}^+ \rightarrow c\text{H}_2\text{O} + d\text{I}_2$   
 In balanced equation, value of  $a + b + c + d$  is \_\_\_\_.

14. In a reaction at equilibrium 'x' moles of the reactant A decomposes to give 1 mole each of C and D. If the fraction of A decomposed at equilibrium is independent of initial concentration of A, then the value of 'x' is \_\_\_\_.
15. To which period does element of atomic number 47 belong?

### SOLUTIONS

1. (c)
2. (c) : Millimoles of A =  $100 \times 0.1 = 10$   
 Millimoles of B =  $25 \times 0.2 = 5$   
 Total millimoles =  $10 + 5 = 15$   
 $\therefore M = \frac{15}{100 + 25} = \frac{15}{125} = 0.12$
3. (b)
4. (b) :  $\text{EtC}\equiv\text{CH} \xrightarrow[\text{THF}]{\text{BD}_3} \begin{array}{c} \text{Et} \\ \diagdown \\ \text{C}=\text{C} \\ \diagup \\ \text{D} \end{array} \begin{array}{c} \text{H} \\ \diagdown \\ \text{C} \\ \diagup \\ \text{BD}_2 \end{array}$   
 $\xrightarrow{\text{CH}_3\text{COOH}} \begin{array}{c} \text{Et} \\ \diagdown \\ \text{C}=\text{C} \\ \diagup \\ \text{D} \end{array} \begin{array}{c} \text{H} \\ \diagdown \\ \text{C} \\ \diagup \\ \text{P} \end{array} \text{H}$
5. (c)
6. (a) :  $E_n = -\frac{E_1}{n^2} \times Z^2$   
 $E_{\text{He}^+} = E_{\text{H}} \times 2^2$ ;  $E_{\text{Li}^{2+}} = E_{\text{H}} \times 3^2$
7. (d) : Hybridisation :  $sp^3$        $sp^2$        $sp$   
 % of s character :      25      33      50  
 $\therefore$  The order of increasing s-character  
 $\text{BF}_4^- (sp^3) < \text{BF}_3 (sp^2) < \text{BF}_2^+ (sp)$
8. (a)
9. (b) :  $\text{Be}_2\text{C} + 4\text{H}_2\text{O} \longrightarrow 2\text{Be}(\text{OH})_2 + \text{CH}_4$   
 $\text{Be}(\text{OH})_2 + 2\text{HCl}_{(aq)} \longrightarrow \text{BeCl}_{2(aq)} + 2\text{H}_2\text{O}$
10. (b) : Element : C      Si      Ge      Sn      Pb  
 EN:      2.5      1.8      1.8      1.8      1.9

### MONTHLY TEST DRIVE CLASS XII ANSWER KEY

1. (d)    2. (d)    3. (a)    4. (c)    5. (d)  
 6. (b)    7. (b)    8. (b)    9. (a)    10. (c)  
 11. (a)    12. (a)    13. (b)    14. (b)    15. (c)  
 16. (b)    17. (c)    18. (b)    19. (d)    20. (a, c)  
 21. (a, b)    22. (a, d)    23. (a, c)    24. (2)    25. (6.8)  
 26. (1.62)    27. (b)    28. (b)    29. (a)    30. (c)



11. (100) :  $2.303 \log \frac{P_2}{P_1} = \frac{\Delta H}{R} \frac{[T_2 - T_1]}{T_1 T_2}$

$\therefore 2.303 \log \frac{10}{1} = \frac{460.6}{2} \times \frac{[T_2 - 50]}{50 \times T_2}$

$\Rightarrow T_2 = 100 \text{ K}$

12. (4.344) : For  $\text{H}_2\text{O}$  vapours,  $PV = nRT$

$\frac{27}{760} \times 2.5 \times 10^4 = n \times 0.0821 \times 300 \Rightarrow n = 36.1$

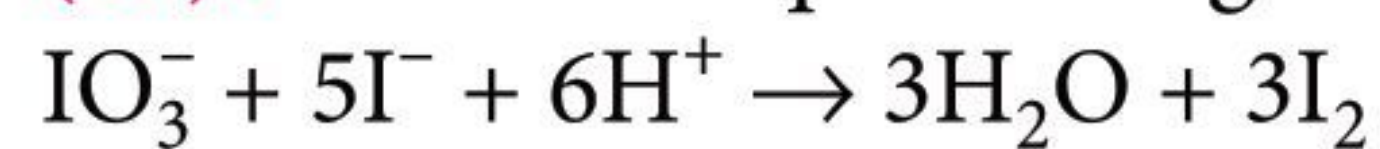
$\therefore$  Mass of  $\text{H}_2\text{O}$  in the form of vapours  
 $= 36.1 \times 18 = 649.8 \text{ g}$

$\therefore$  Volume of  $\text{H}_2\text{O}_{(l)}$  evaporated

$= \frac{649.8}{0.990} = 656.4 \text{ mL}$

$\therefore$  Volume of  $\text{H}_2\text{O}_{(l)}$  left  $= (5.0 - 0.6564) = 4.344 \text{ L}$

13. (17) : Balanced equation is given as :



$a = 5, b = 6, c = 3, d = 3$

$a + b + c + d = 5 + 6 + 3 + 3 = 17$

14. (2) :  $x\text{A} \rightleftharpoons \text{C} + \text{D}$

Initial  $a \quad 0 \quad 0$

At eqm.  $a(1 - \alpha) \quad \frac{a\alpha}{x} \quad \frac{a\alpha}{x}$

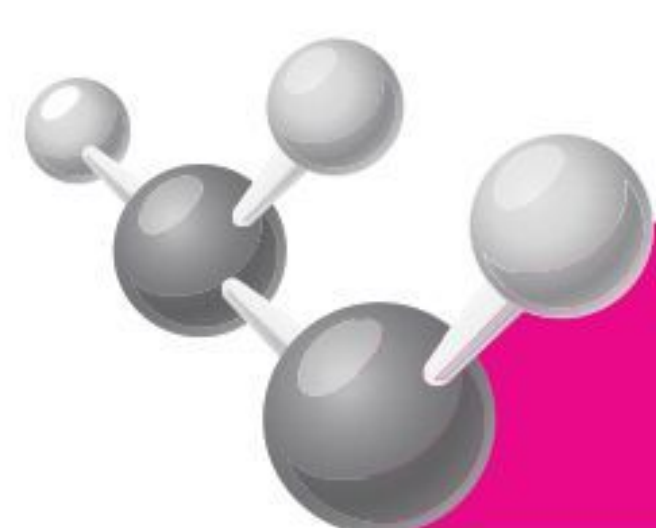
$\therefore K = \frac{[\text{C}][\text{D}]}{[\text{A}]^x} = \frac{\frac{a^2\alpha^2}{x^2V^2}}{\frac{[a(1-\alpha)]^x}{V^x}} = \frac{a^{(2-x)}\alpha^2}{x^2(1-\alpha)^x V^{x-2}}$

If  $\alpha$  is independent of  $a$ , then  $2 - x = 0$

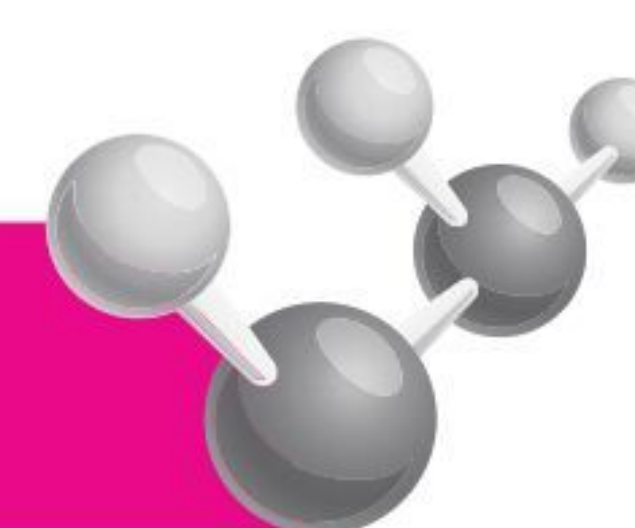
$\therefore x = 2$

15. (5) : Electronic configuration  $= [\text{Kr}]4d^{10}5s^1$

Period  $= 5^{\text{th}}$



## 3 Amazing Researches You Must Know



### 1. Newly Discovered Effects of a Natural Medicine with One Thousand Years of History

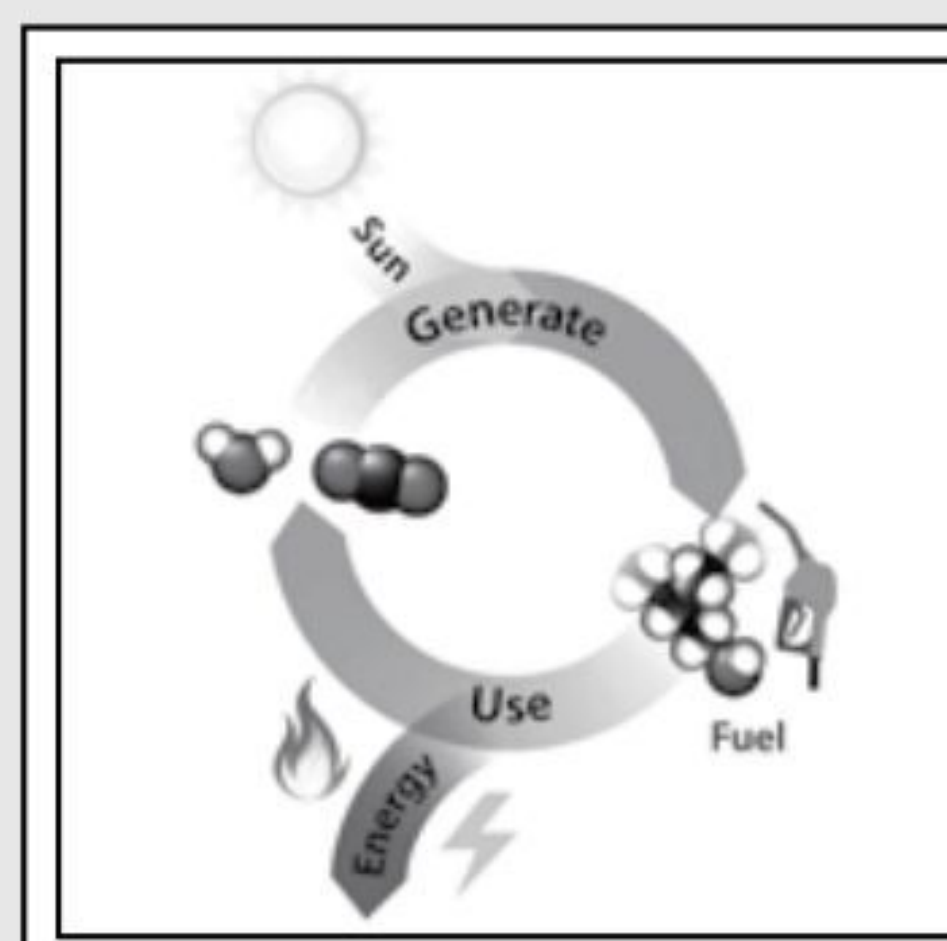
Recently research has been carried out at the University of Warwick into an 'antibiotic' vegetable paste whose recipe is 1,000 years old. It is called 'vision repairing ointment', and it was discovered in the Old English medical manual *Medicanale Anglicum*, written in the 9<sup>th</sup> century. The ointment, which contains onions, garlic (or leek – the scientists had trouble translating the name correctly), cow bile and wine, has extremely potent antiseptic properties. It has been shown to be effective against certain strains of bacteria that have become resistant to modern drugs.

Even initial testing has proven the concoction's effectiveness in treating *Staphylococcus aureus*. However, recent research has been extended to other strains and the results have been presented in the form of a scientific publication. Experiments have shown that this natural medicine can be a powerful weapon against bacteria called biofilms.



### 2. Sunlight for Fuel Production

Researchers have discovered a method that can transform plastic waste into chemicals by using sunlight. A team of scientists conducted research on a mixture of plastics with their catalyst in a solvent, which allows the use of light energy. As a result, dissolved plastics were transformed into formic acid. This acid is used in fuel cells to produce electricity. This discovery is aimed at developing sustainable methods of using sunlight to produce fuels and other chemical products.



### 3. Diamonds Made in Minutes

Scientists managed to create a diamond just by applying high pressures and without raising the ambient temperature. They obtained two types of diamond. One was a typical stone, which could be used on a ring after cutting. The second type was called lonsdaleite, a form which is found in nature after a meteorite hits the Earth. The possibility of creating a diamond so quickly and at room temperature opens up multiple possibilities, including for industry.

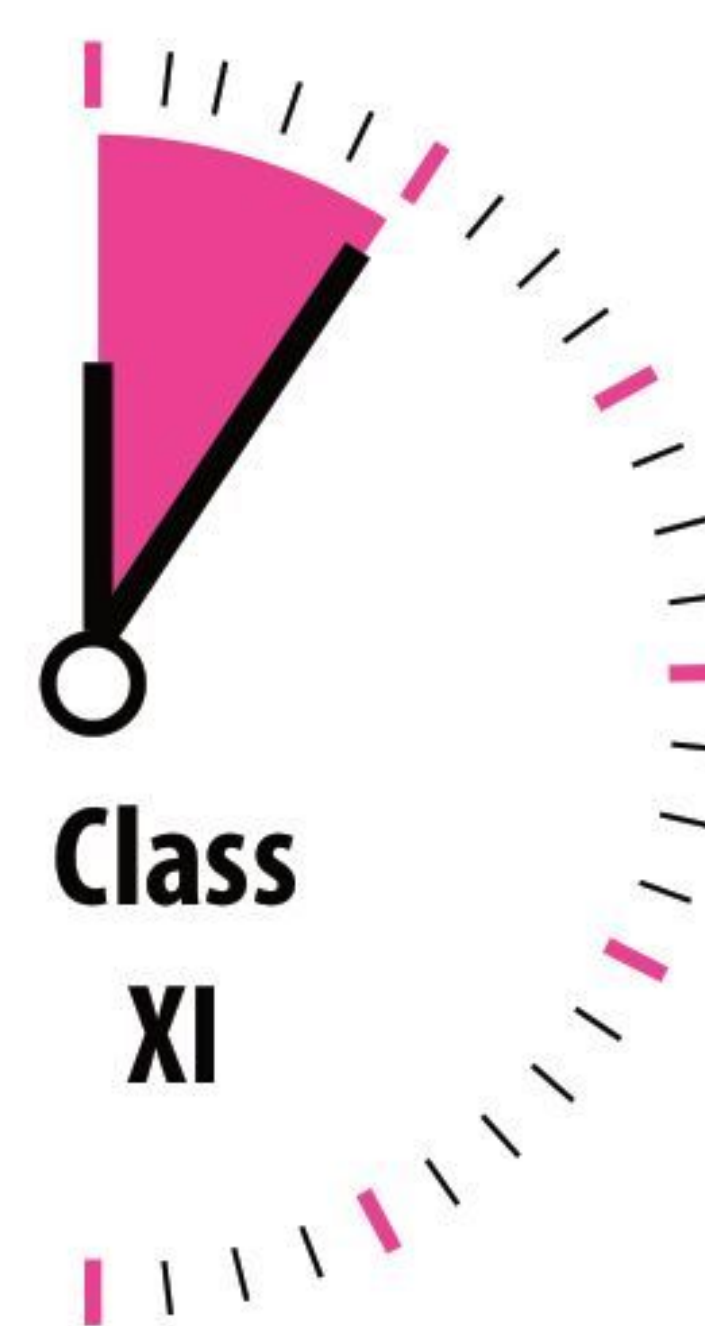




# LEARNFAST

## ESSENTIALS FOR TERM-II

### States of Matter : Gases and Liquids | Chemical Thermodynamics | Equilibrium



#### STATES OF MATTER : GASES AND LIQUIDS

##### Gas Laws

- ◆ **Boyle's Law** :  $V \propto \frac{1}{P}$  at constant temperature

or  $PV = \text{constant}$

$$\boxed{P_1 V_1 = P_2 V_2}$$

(Initial state) (Final state)

- ◆ **Charles' Law** :  $V_t = V_0 + \frac{V_0}{273} \times t$   
(at constant pressure)

$V_t \propto T$  or simply  $V \propto T$

i.e.,  $\frac{V}{T} = \text{constant}$  (at constant pressure)

or  $\boxed{\frac{V_1}{T_1} = \frac{V_2}{T_2}}$

- ◆ **Gay-Lussac's Law** :  $P \propto T$  (at constant volume)

$\frac{P}{T} = \text{constant}$  or  $\boxed{\frac{P_1}{T_1} = \frac{P_2}{T_2}}$  (at constant volume)

- ◆ **Avogadro's law** : Equal volume of all gases under similar conditions of temperature and pressure contain equal number of molecules.

##### Ideal Gas Equation

- ◆  $\frac{PV}{T} = \text{constant}$  or  $\boxed{\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}}$   
or  $\boxed{PV = nRT}$

$$P = \frac{m}{V} \frac{RT}{M} = \frac{dRT}{M} \text{ or } \boxed{M = \frac{dRT}{P}}$$

$\frac{dT}{P} = \frac{M}{R}$ , since  $M$  and  $R$  are constant for a gas.

$$\therefore \frac{dT}{P} = \text{constant}$$

$$\therefore \boxed{\frac{d_1 T_1}{P_1} = \frac{d_2 T_2}{P_2}}$$

- ◆ **Value of gas constant ( $R$ )**

$$\begin{aligned} R &= 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1} \\ &= 8.314 \times 10^7 \text{ ergs K}^{-1} \text{ mol}^{-1} \\ &= 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \\ &= 1.987 \text{ cal K}^{-1} \text{ mol}^{-1} \end{aligned}$$

##### Dalton's Law of Partial Pressure

$$\boxed{P_{\text{Total}} = p_A + p_B + p_C + \dots}$$

- ◆ **Partial Pressure** :

Partial pressure = Mole fraction  $\times$  Total pressure

$$p_i = x_i \times P_{\text{Total}}$$

##### Graham's Law of Diffusion

- ◆  $r_{\text{diffusion}} \propto \sqrt{\frac{1}{d}}$  ;  $\boxed{\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}}}$  (At same pressure)

Since, molecular mass ( $M$ ) =  $2 \times$  vapour density

$$\boxed{\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}}$$

##### Ideal and Real gases

- ◆ A gas which obeys gas laws or simply ideal gas equation ( $PV = nRT$ ) under all conditions of temperature and pressure is called **ideal gas**. However, no gas is found to be ideal. The concept of ideal gas is only theoretical. The gases are found to obey gas laws at low pressure and high temperature. Such gases are known as **real gases**. All gases are real gases.

##### Cause of Deviation

- ◆ There are two faulty assumptions of kinetic theory because of which gases deviate from ideal behaviour.



- The actual volume occupied by the molecules of a gas is negligible in comparison to total volume of the gas.
- There are no forces of attraction or repulsion between the gas molecules. Under the conditions of high pressure and low temperature, the forces of attraction or repulsion between the molecules and size of molecule may not be negligible.

### Compressibility Factor

◆  $Z = \frac{PV_{\text{real}}}{RT}$   
 For ideal gas,  $Z = 1$ ,  $V_{\text{ideal}} = \frac{RT}{P}$   
 Putting  $\frac{RT}{P}$  in above equation,  $Z = \frac{V_{\text{real}}}{V_{\text{ideal}}}$

### van der Waals' Equation for Real Gases

- ◆ van der Waals' gave modified form of ideal gas equation applicable to real gases.

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT, \text{ for } n \text{ moles of a gas}$$

### Questions for Practice

1. In terms of Charles' law, explain why  $-273^\circ\text{C}$  is the lowest temperature? (NCT 2015, 2016, KVS 2016)
2. Using the equation of state  $PV = nRT$ ; show that at a given temperature, density of a gas is proportional to gas pressure  $P$ . (NCERT, KVS 2015)
3. Calculate the total pressure in a mixture of 8 g of oxygen and 4 g of hydrogen confined in a vessel of  $1 \text{ dm}^3$  at  $27^\circ\text{C}$ .  $R = 0.083 \text{ bar dm}^3 \text{ K}^{-1} \text{ mol}^{-1}$ . (NCERT, NCT 2011, 2014, 2015, 2016)
4. Write van der Waals' equation for one mole of a gas. (NCT 2011, KVS 2014)

## CHEMICAL THERMODYNAMICS

**System :** The part of universe under thermodynamic study is called system.

**Surrounding :** The part of universe other than the system is known as surrounding.

### State Function

- ◆ Depends only on the state of the system (initial and final) and independent of the path by which this state has been attained. For example : potential energy, internal energy, enthalpy, free energy, pressure, volume, temperature, etc.

### Thermodynamic Properties

- ◆ **Extensive properties :** Depend upon the amount of matter contained in a system. For example: mass, volume, enthalpy, entropy, free energy, heat capacity, etc.
- ◆ **Intensive properties :** Do not depend upon the amount of matter present in the system but depend only on the nature of the matter. For example: temperature, pressure, density, refractive index, viscosity, specific heat, freezing point, boiling point, etc.

### Thermodynamic Processes

- ◆ There are various type of processes according to the conditions applied :
- Isothermal Process *i.e.*,  $\Delta T = 0$
  - Adiabatic Process *i.e.*,  $\Delta q = 0$
  - Isobaric Process *i.e.*,  $\Delta P = 0$
  - Isochoric Process *i.e.*,  $\Delta V = 0$

### (a) Work (W)

- ◆ Work = Pressure  $\times$  area  $\times l = P_{\text{ext}} \times \Delta V$   
 (area  $\times l$  = Volume)
- ◆ **Sign convention :** If work is done by the system, it is taken as negative, whereas if work is done on the system, it is taken as positive.

$$\text{For expansion, } W = -P_{\text{ext}} \Delta V$$

$$\text{For contraction, } W = P_{\text{ext}} \Delta V$$

- ◆ If irreversible expansion takes place against vacuum, the process is called free expansion. For such expansion,  $W = 0$  as  $P_{\text{ext}} = 0$ .
- ◆ Work done for isothermal reversible expansion

$$W = -2.303nRT \log \frac{V_2}{V_1}$$

or  $W = -2.303nRT \log \frac{P_1}{P_2}$

### (b) Heat (q)

- ◆ Mode of energy transfer between system and surrounding because of temperature difference between them.  
 SI unit of heat is Joule.  
 $1 \text{ Calorie} = 4.184 \text{ Joules}$ , *i.e.*,  $1 \text{ Joule} = 0.2390 \text{ Calorie}$ ,  
 $1 \text{ L atm} = 101.3 \text{ J} = 24.206 \text{ Calories}$
- ◆ **Sign convention :** It is taken as negative when heat is given by the system to the surrounding. Whereas when heat is absorbed by the system from surrounding, it is taken as positive.



### (c) Internal Energy ( $U$ or $E$ )

- ◆ The total energy stored in a substance (or a system) is called its internal energy.

$$\Delta U = U_2 - U_1 \quad \text{or} \quad \Delta U = U_{\text{product}} - U_{\text{reactant}}$$

### First Law of Thermodynamics

- ◆  $\Delta E$  or  $\Delta U = q + W$  or  $q = \Delta U - W$ 
  - If  $W$  is work of expansion *i.e.*,  $W = -P\Delta V$  then  $\Delta U = q - P\Delta V$  or  $q = \Delta U + P\Delta V$
  - For isothermal irreversible expansion,  $\Delta U = 0$  thus,  $q = -W = P\Delta V$
  - For isothermal reversible expansion,
$$\Delta U = 0 \text{ thus, } q = -W = 2.303nRT \log \frac{V_2}{V_1}$$
  - For adiabatic processes,  $q = 0$  thus,
$$\Delta U = W_{\text{adiabatic}}$$
$$\frac{dU}{dT} = C_V \Rightarrow dU = C_V dT$$
Thus,  $W_{\text{adiabatic}} = C_V dT = C_V (T_2 - T_1)$
  - For isochoric process,  $\Delta V = 0$  thus,  $q = \Delta U$

### Enthalpy ( $H$ )

- ◆ Total heat content of the system at constant pressure is known as its enthalpy.

Mathematically,  $H = U + PV$

$$\Delta H = \Delta U + P\Delta V$$

### Heat of Reaction at Constant Pressure and at Constant Volume

- ◆ According to 1<sup>st</sup> law of thermodynamics,
$$q = \Delta U - W$$
$$W = -P\Delta V$$
At constant volume,  $\Delta V = 0$ ,  $W = 0$ Thus,  $q_V = \Delta U$ At constant pressure,  $W = -P\Delta V$ 
$$q_P = \Delta U + P\Delta V$$
Comparing this equation with equation of enthalpy change.
$$q_P = \Delta H$$

- ◆ **Relationship between  $\Delta H$  and  $\Delta U$**

We know that  $\Delta H = \Delta U + P\Delta V$

$$\therefore \Delta H = \Delta U + P(V_2 - V_1) = \Delta U + (PV_2 - PV_1)$$

For ideal gases,  $PV = nRT$

Thus we have,  $PV_1 = n_1RT$  and  $PV_2 = n_2RT$

$$\Delta H = \Delta U + (n_2RT - n_1RT)$$

$$\Delta H = \Delta U + \Delta n_g RT$$

### Heat of Reaction ( $\Delta H$ )

- ◆ It is the heat evolved or absorbed during the reaction.

$$\Delta H = \sum \Delta H_{\text{Product}} - \sum \Delta H_{\text{Reactant}}$$

If  $\sum \Delta H_P > \sum \Delta H_R$ ,  $\Delta H = +ve$  *i.e.*, endothermic reaction

If  $\sum \Delta H_R > \sum \Delta H_P$ ,  $\Delta H = -ve$  *i.e.*, exothermic reaction

Heat of reaction is also known as enthalpy of reaction.

$$\Delta H_{\text{Reaction}}^{\circ} = \Delta H_{f(\text{Products})}^{\circ} - \Delta H_{f(\text{Reactants})}^{\circ}$$

### Hess's Law of constant heat summation

- ◆ Heat change accompanying a chemical reaction is same whether the reaction takes place in a single step or in a number of steps.

### Second Law of Thermodynamics

- ◆ There are many statements for 2<sup>nd</sup> law.
  - All spontaneous processes are thermodynamically irreversible.
  - It is impossible to convert heat completely into equivalent amount of work without leaving some effect elsewhere.
  - Without the help of an external agency, heat can not by itself flow from a cold body to hot body.
  - The entropy of the universe is continuously increasing.

### Entropy ( $S$ )

- ◆ Entropy is defined as a measure of randomness or disorder of the system. It is denoted by  $S$ . It is a state function.

$$\Delta S = \frac{q_{\text{rev}}}{T}$$

$$\Delta S = S_2 - S_1 = \sum S_{\text{Products}} - \sum S_{\text{Reactants}}$$

For a reversible process at equilibrium  $\Delta S = 0$

$$\Delta S_{\text{Total}} = \Delta S_{\text{System}} + \Delta S_{\text{Surrounding}}$$

For a process to be spontaneous

$$\Delta S_{\text{Total}} = \Delta S_{\text{System}} + \Delta S_{\text{Surrounding}} > 0$$

### Units of Entropy Change

- ◆  $\Delta S = \frac{q}{T}$ ; thus  $\Delta S$  is  $\text{J K}^{-1} \text{mol}^{-1}$ . It is an extensive property.

### Spontaneous Process

- ◆ A process which takes place by itself or after proper initiation under a given set of conditions. Spontaneous processes are irreversible.



- ◆ An increase in entropy or randomness (*i.e.*, positive  $\Delta S$ ) favours the spontaneity of a reaction.

### Free energy ( $G$ )

- ◆ Free energy change is given as,  $\Delta G = \Delta H - T\Delta S$
- ◆ This expression combines both energy factor ( $\Delta H$ ) and entropy factor ( $\Delta S$ ) of spontaneity. It means  $\Delta G$  is resultant of two factors.
- ◆ For a reaction to be spontaneous  $\Delta G$  must be negative.
- ◆ If  $\Delta G = 0$ , process is in equilibrium and if  $\Delta G = \text{positive}$ , process is non-spontaneous.

### Third Law of Thermodynamics

- ◆ This law states that entropy of all perfectly crystalline solids approaches zero at absolute zero temperature (zero Kelvin). Entropy is a measure of disorder, hence it can be said that at absolute zero a perfectly crystalline solid has a perfect order of its constituent particles.

$$\Delta S = S_T - S_0 = \int_0^T \frac{C_P dT}{T} = C_P \ln T = 2.303 C_P \log T$$

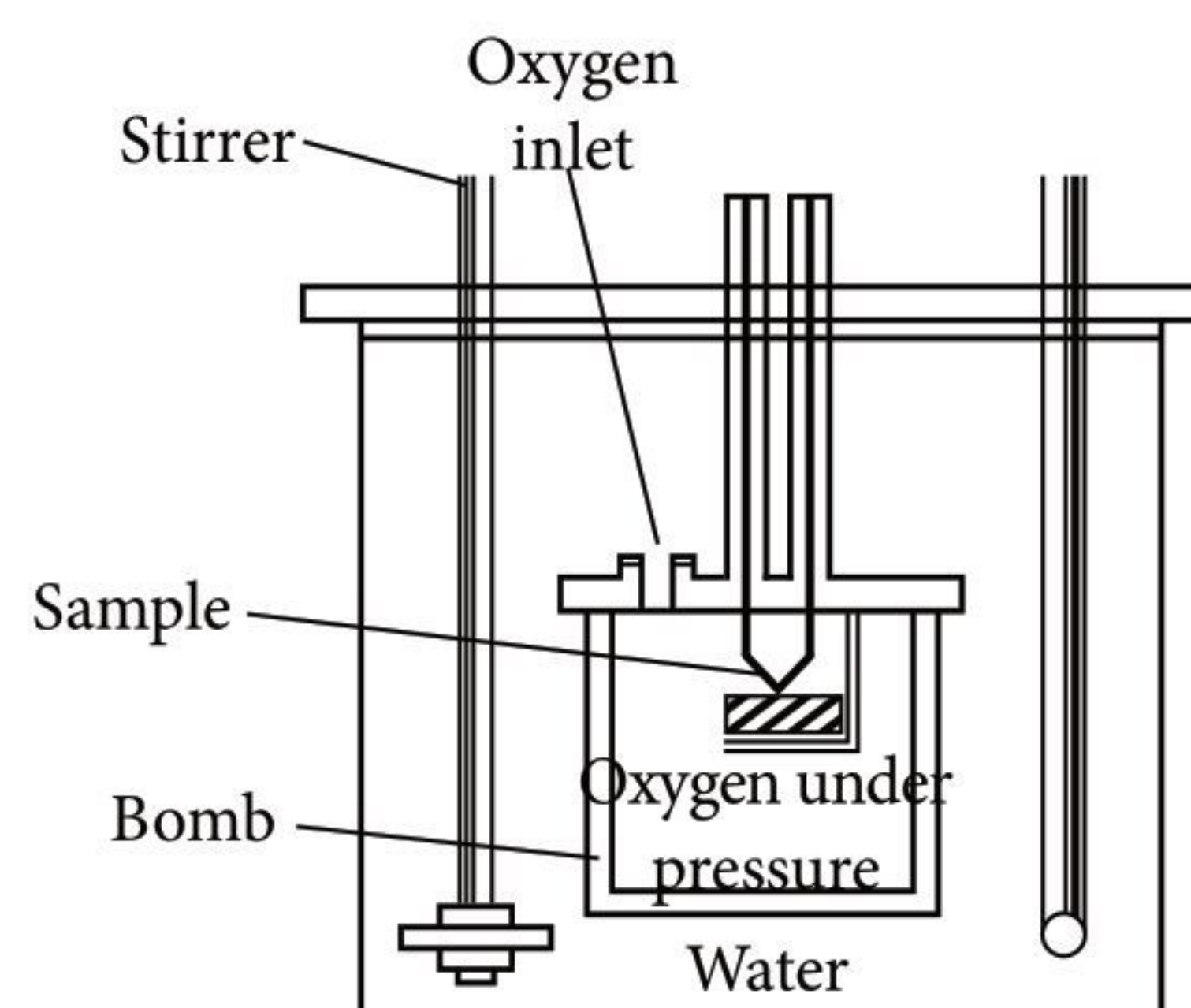
As  $S_0 = 0$

$$\therefore S_T = \int_0^T \frac{C_P dT}{T}$$

### Questions for Practice

- In a process, 701 J of heat is absorbed by a system and 394 J of work is done by the system. What is the change in internal energy for the process?  
(NCERT, NCT 2017)
- Name any two intensive properties. (KVS 2016)
- (a) Give one point to differentiate between the following thermodynamic terms : Extensive and intensive property.  
(b) If water is assumed to be a perfect gas, molar enthalpy change for vapourisation of 1 mole of water at 1 bar and 100°C is 41 kJ/mole. Calculate the internal energy change when 1 mole of water is vapourised at 1 bar pressure and 100°C.  
(KVS 2014)

- (a) What does the following diagram indicate?  
(b) What for it is used?



(KVS 2013, 2014)

- (a) Calculate the standard enthalpy of formation of  $C_2H_{4(g)}$  from the following thermochemical equation :  

$$C_2H_{4(g)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 2H_2O_{(g)} ; \quad \Delta H^\circ = -1323 \text{ kJ}$$
 Given that  $\Delta_f H^\circ$  of  $CO_{2(g)}$ ,  $H_2O_{(g)}$  as  $-393.5$  and  $-249 \text{ kJ mol}^{-1}$  respectively.  
 (b) State Hess's law of constant heat summation.  
(KVS 2016)
- The standard free energy of a reaction is found to be zero. What is its equilibrium constant?  
(KVS 2016)

## EQUILIBRIUM

### Physical Equilibrium

- ◆ Physical equilibrium generally exists between different states of substance at a particular temperature,  

$$\text{Solid} \rightleftharpoons \text{Liquid}, \text{Liquid} \rightleftharpoons \text{Gas}, \text{Solid} \rightleftharpoons \text{Gas}$$

### Henry's Law

- ◆ States that the mass of a gas ( $m$ ) dissolved in a given mass of a solvent at any temperature is directly proportional to the partial pressure ( $p$ ) of the gas above the solvent.  

$$m \propto p \text{ or } m = kp$$
 where,  $k$  is a constant of proportionality known as **Henry's constant**.

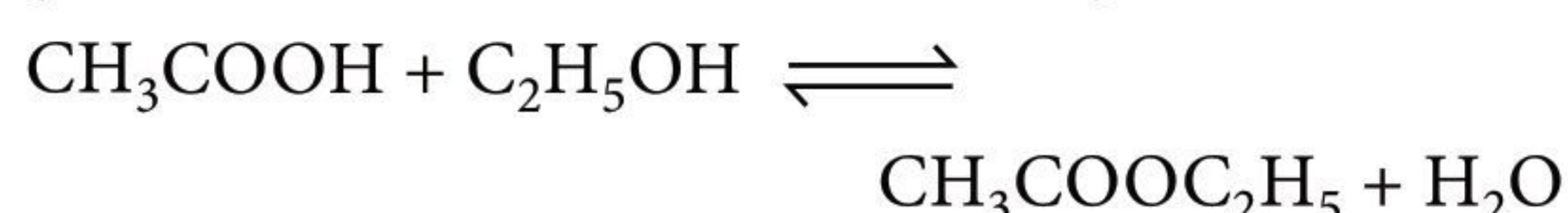


## Chemical Equilibrium

- Chemical reactions are broadly divided into two categories.

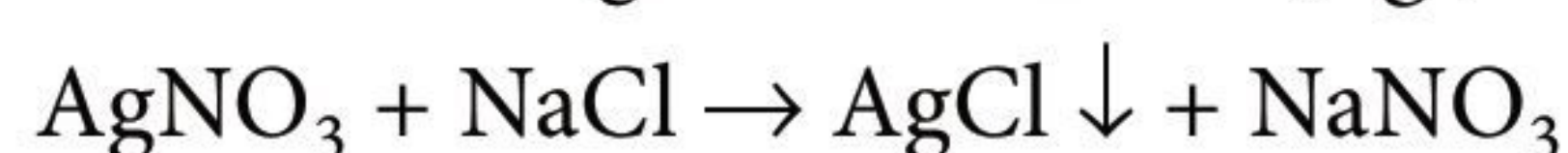
### (i) Reversible Reaction

A reaction in which the reactants are formed back by the reaction of products with each other at the given conditions of the reaction. *e.g.*,



### (ii) Irreversible Reaction

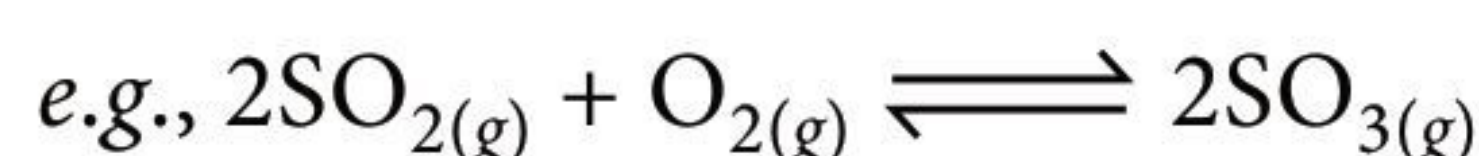
These are the reactions in which products do not react back to give the reactants, *e.g.*,



## Types of Chemical Equilibrium

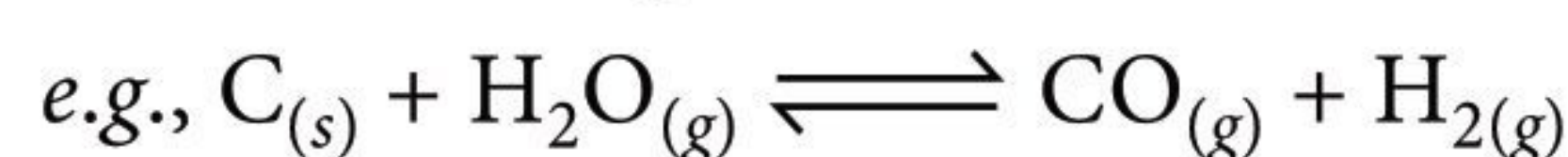
### (i) Homogeneous Equilibrium

All the reactants and products are present in same phase.



### (ii) Heterogeneous Equilibrium

Reactants and products are present in two or more than two different phases.



## State of Equilibrium

- Chemical equilibrium is the state of a reaction at which the rate of forward reaction becomes equal to rate of backward reaction.

## Law of Mass Action

- $aA + bB \rightleftharpoons cC + dD$

According to the law of mass action,

Rate of forward reaction,  $r_f \propto [A]^a [B]^b$

Rate of backward reaction,  $r_b \propto [C]^c [D]^d$

- At equilibrium,

Rate of forward reaction = Rate of backward reaction,

$$k_f [A]^a [B]^b = k_b [C]^c [D]^d$$

$$\text{or } \frac{[C]^c [D]^d}{[A]^a [B]^b} = \frac{k_f}{k_b} = K \text{ or } K_c$$

= Equilibrium constant

## Relationship between $K_p$ and $K_c$

- $K_p$  and  $K_c$  are related as

$$K_p = K_c (RT)^{\Delta n_g}$$

$\Delta n_g$  = Change in number of gaseous moles = Number of gaseous moles of product – Number of gaseous moles of reactants

## Characteristics of Equilibrium Constant

- If the reaction is reversed, the value of equilibrium constant is inversed.

$$K' = \frac{1}{K}$$

- When the equation for a reaction is divided by a factor ' $n$ ', the value of new equilibrium constant becomes equal to  $n^{\text{th}}$  root of the previous equilibrium constant.

$$K' = \sqrt[n]{K}$$

- If the equation for a reaction is multiplied by a factor ' $n$ ' then the new equilibrium constant ( $K'$ ) becomes  $K^n$ .

$$K' = K^n$$

- If the equation is written in number of steps, then its equilibrium constant will be the multiple of the equilibrium constants of each step.

$$K = K_1 \times K_2 \times K_3 \times \dots$$

## Effect of Temperature on Equilibrium Constant

- Variation of equilibrium constant with temperature is explained with the help of van't Hoff equation.

$$\log \frac{K_2}{K_1} = \frac{\Delta H^\circ}{2.303R} \left[ \frac{T_2 - T_1}{T_1 T_2} \right]$$

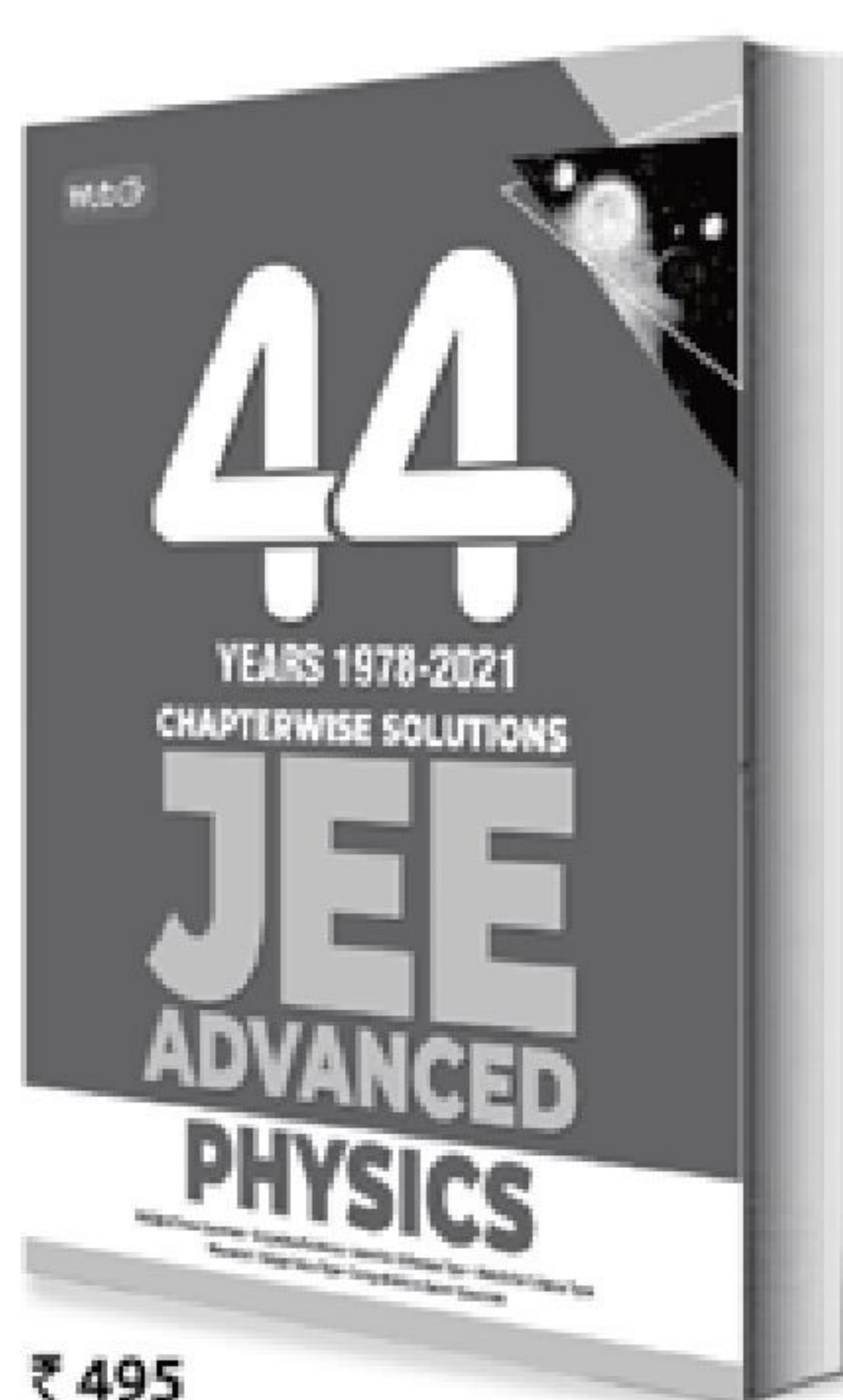
## Le-Chatelier's Principle

- The law states that if any kind of change in concentration, temperature or pressure is imposed on the system in equilibrium, then equilibrium shifts in a direction that tends to undo the effect of the change imposed.

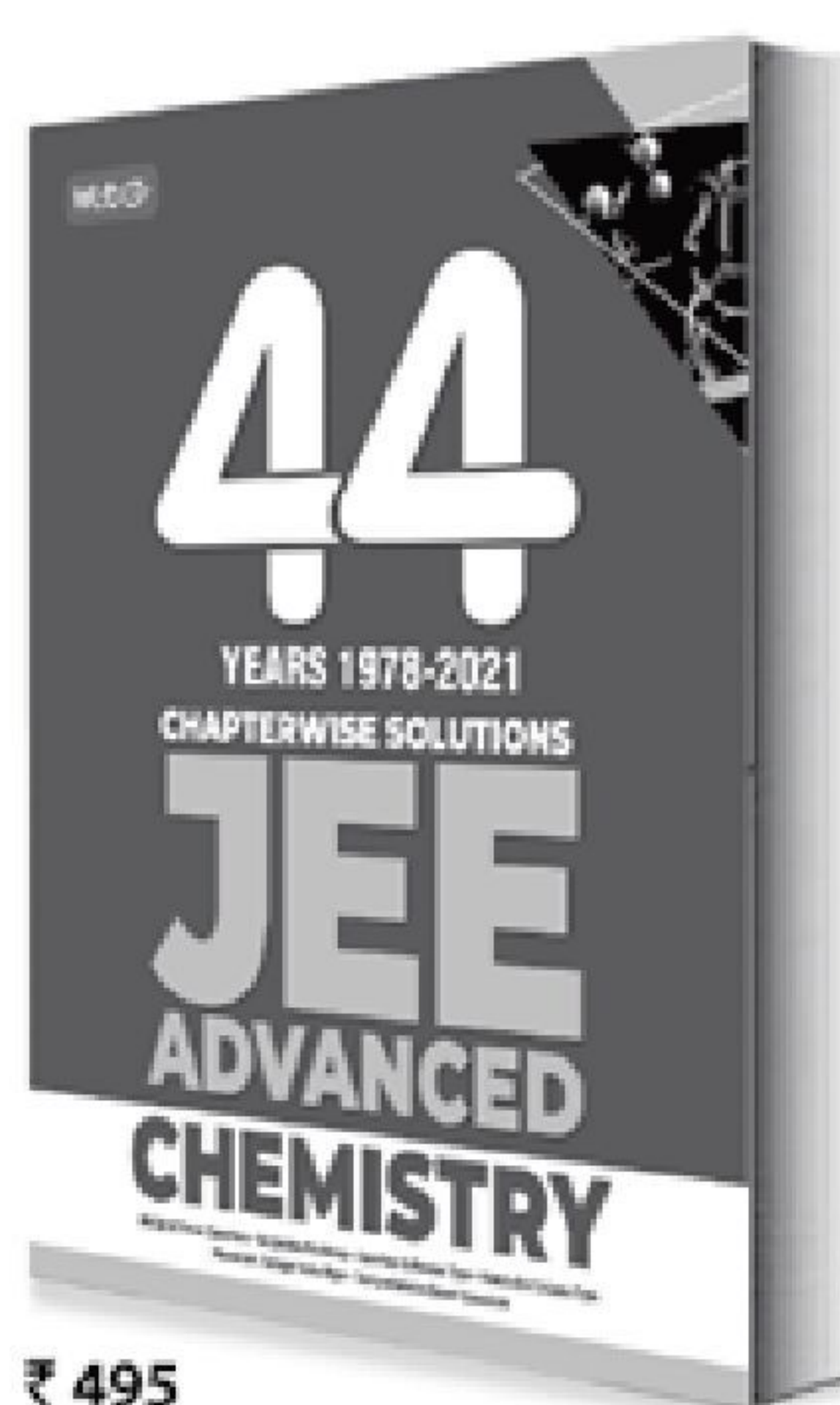




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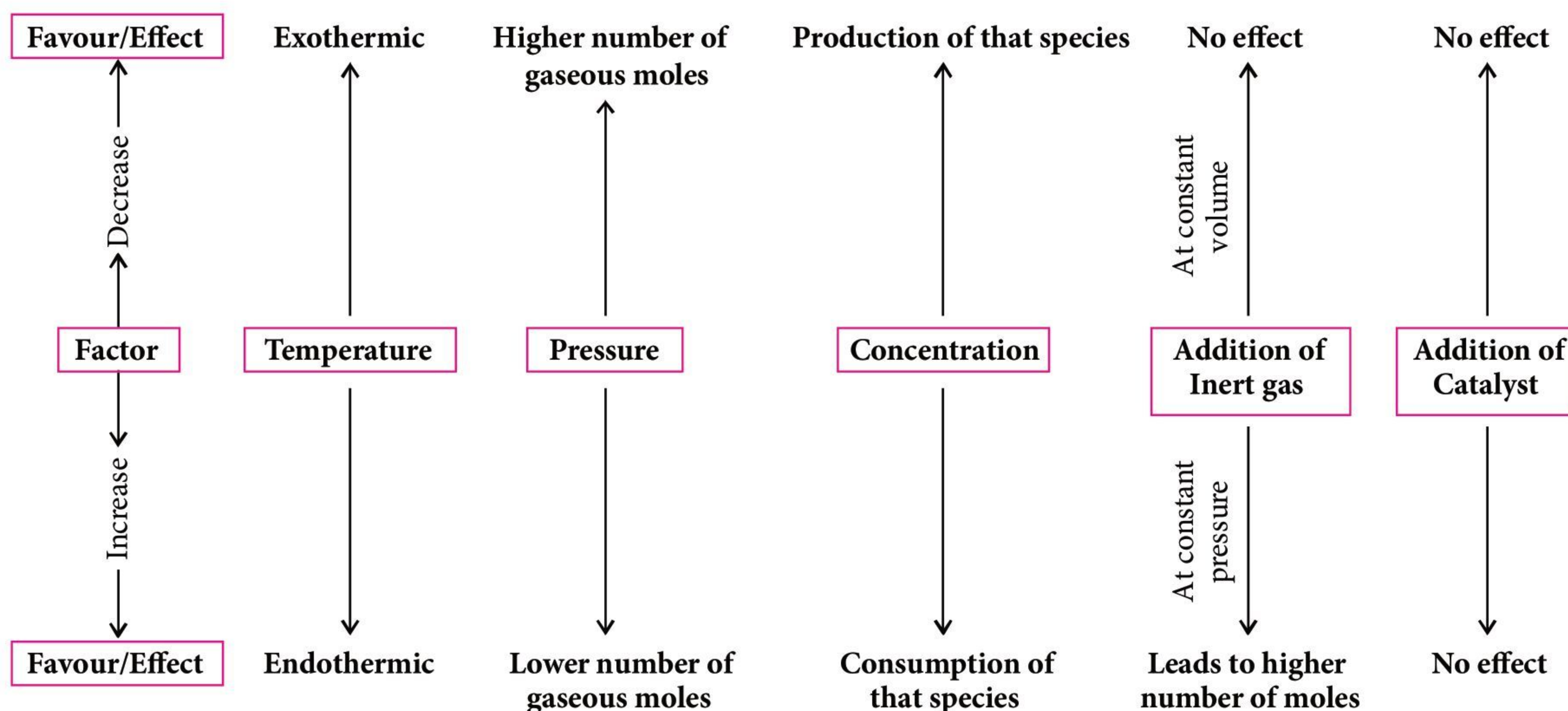
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## Effect of various factors on equilibrium



## Ionic Equilibrium

### Electrolyte and Non-Electrolyte

- ◆ A compound whose aqueous solution or molten state conducts electricity is known as electrolyte, whereas non-electrolyte is the compound which does not conduct electricity in aqueous or molten state.

### Degree of Dissociation ( $\alpha$ )

$$\text{Degree of dissociation, } \alpha = \frac{\text{Number of moles dissociated}}{\text{Total number of moles}}$$

Degree of dissociation is directly proportional to temperature.

### Strong and Weak Electrolytes

- ◆ Electrolytes which dissociate almost completely into ions in aqueous solution are known as strong electrolytes, *e.g.*, NaCl, HCl, NaOH, H<sub>2</sub>SO<sub>4</sub>, etc. They are very good conductors of electricity. They have degree of dissociation nearly one *i.e.*,  $\alpha \approx 1$ . Whereas those electrolytes which dissociate only partially into ions in aqueous solution are known as weak electrolytes, *e.g.*, CH<sub>3</sub>COOH, NH<sub>4</sub>OH, etc.

## Concepts of Acids and Bases

### Arrhenius Concept

- ◆ Arrhenius acid furnishes hydrogen ions in aqueous solution, *e.g.*, HCl.

- ◆ Arrhenius base furnishes hydroxyl ions in aqueous solution, *e.g.*, NaOH.

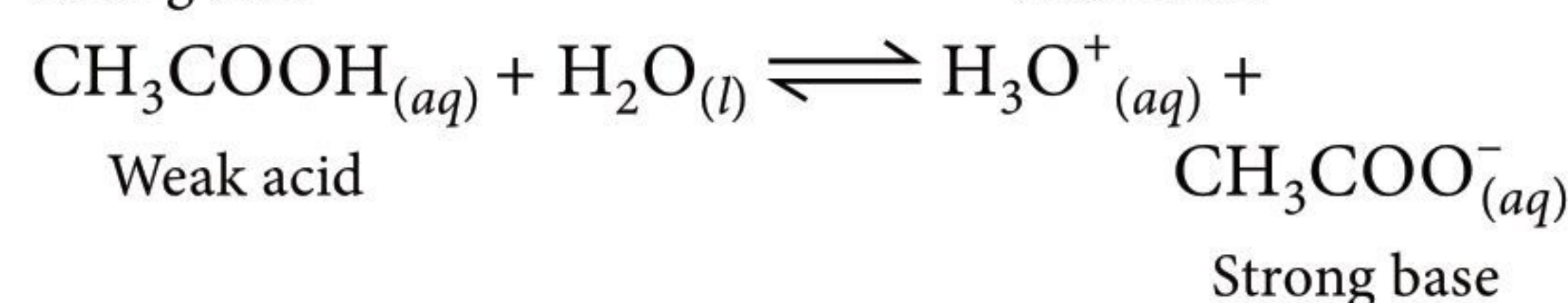
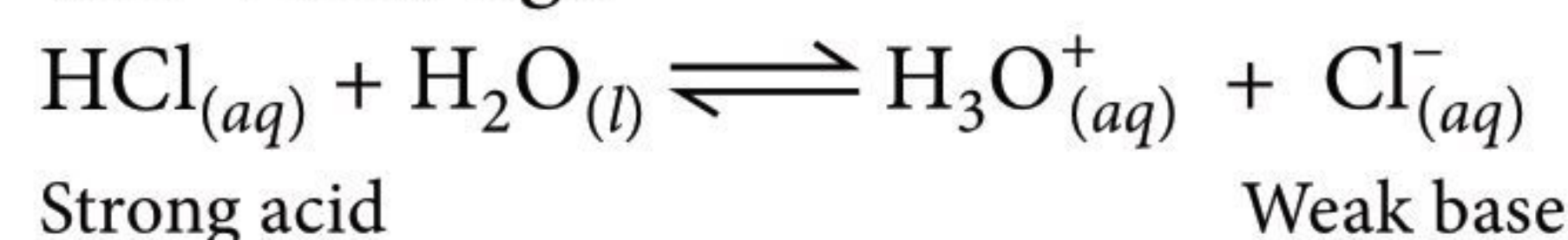
### Brønsted Lowry Concept

- ◆ Brønsted acid donates a proton, *e.g.*, HCl.
- ◆ Brønsted base accepts a proton, *e.g.*, NH<sub>3</sub>.
- ◆ **Conjugate acid - base pairs** : These are the pairs of acids and bases which differ by a proton, *e.g.*,  

$$\text{Acid} \xrightleftharpoons[+H^+]{-H^+} \text{conjugate base}$$

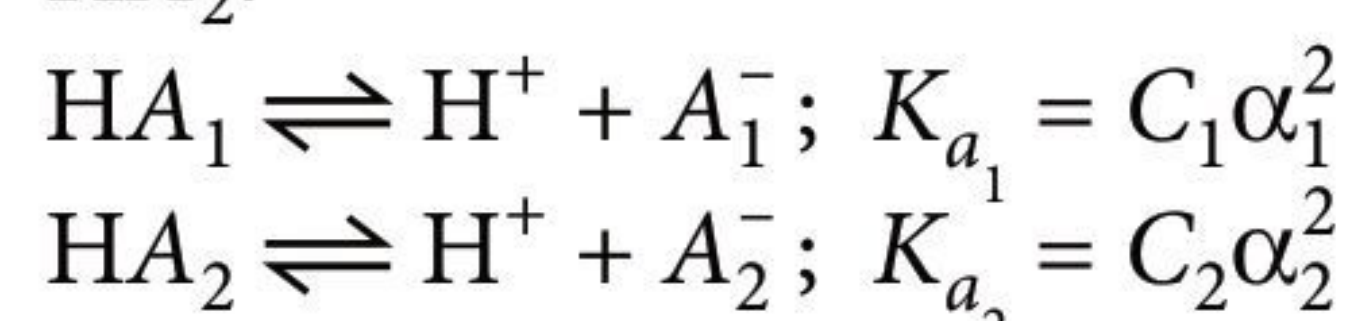
- ◆ Relative strengths of conjugate acids or bases depend upon their tendency to donate a proton or to accept a proton.

- ◆ Stronger the acid, weaker is its conjugate base and vice-versa, *e.g.*,



### Lewis Concept

- ◆ Lewis acid accepts a pair of electrons, *e.g.*, BF<sub>3</sub>.
- ◆ Lewis base donates a pair of electrons, *e.g.*, NH<sub>3</sub>.
- ◆ **Relative strength of acids and bases** : This is the ratio of strengths of acids. *e.g.*, for acids HA<sub>1</sub> and HA<sub>2</sub>:





Relative strength

$$= \frac{[\text{H}^+] \text{ furnished by HA}_1}{[\text{H}^+] \text{ furnished by HA}_2} = \frac{C_1 \alpha_1}{C_2 \alpha_2}$$

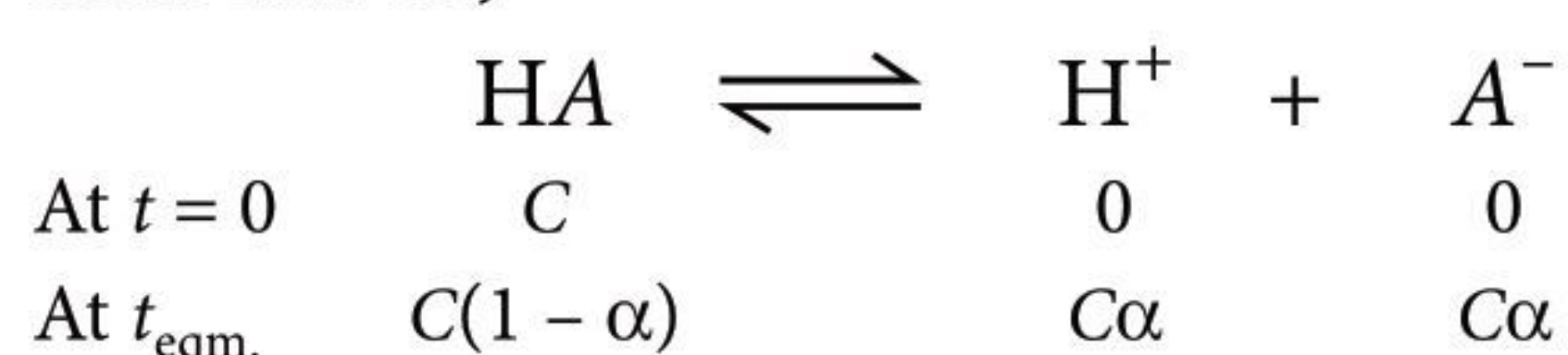
$$(\because \alpha = \sqrt{K_a / C})$$

$$= \frac{C_1 \sqrt{K_{a1}/C_1}}{C_2 \sqrt{K_{a2}/C_2}} = \sqrt{(K_{a1} C_1) / (K_{a2} C_2)}$$

If concentrations of acids are same, then

$$\text{Relative strength} = \sqrt{\frac{K_{a1}}{K_{a2}}}$$

- ◆ **Dissociation constant of weak acids and weak bases :** Let us consider the dissociation of a weak acid HA as,



Dissociation constant of acid,

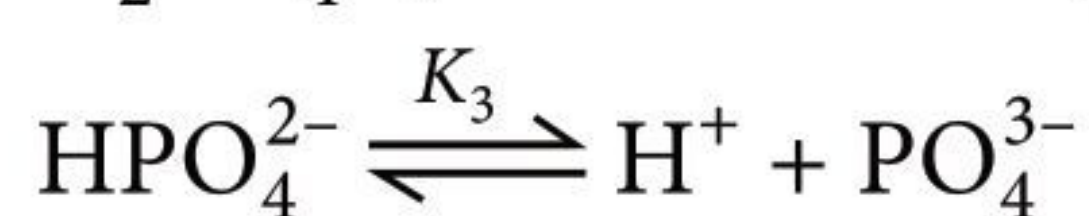
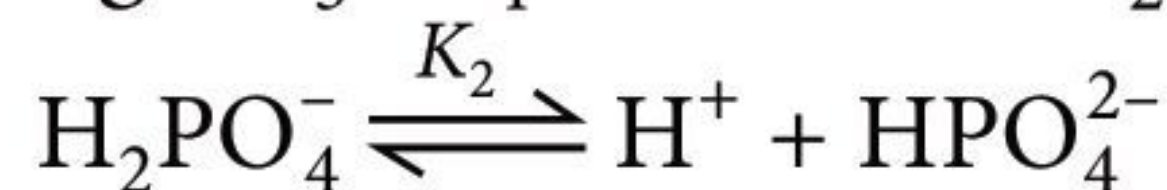
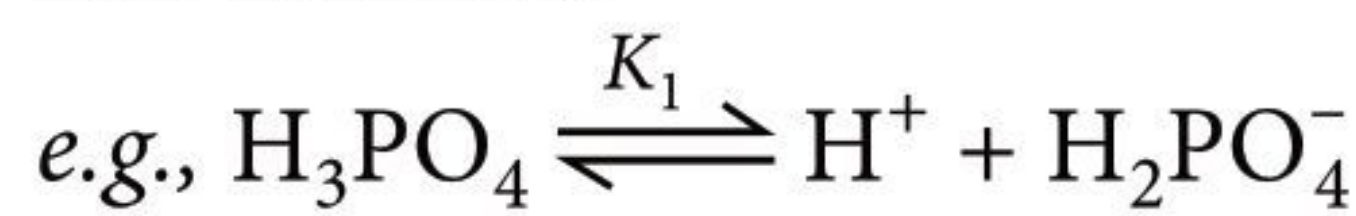
$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{C\alpha \cdot C\alpha}{C(1 - \alpha)} = \frac{C\alpha^2}{(1 - \alpha)}$$

Similarly, for the dissociation of a weak base BOH as  $\text{BOH} \rightleftharpoons \text{B}^+ + \text{OH}^-$

Dissociation constant of base,

$$K_b = \frac{[\text{B}^+][\text{OH}^-]}{[\text{BOH}]} = \frac{C\alpha^2}{(1 - \alpha)}$$

- ◆ **Dissociation constant for polyprotic acids and bases :** These acids involve number of steps to ionise completely, where number of steps is equal to the number of replaceable hydrogen atoms. The value of ionisation constant of each step is definite and constant



The overall dissociation constant ( $K$ ) is given as

$$K = K_1 \times K_2 \times K_3 \text{ where } K_1 > K_2 > K_3.$$

## Concept of pH

- ◆ pH is a convenient method to represent hydrogen ion concentration. pH of a solution is defined as, the negative logarithm of hydrogen ion concentration.

$$\boxed{\text{pH} = -\log [\text{H}^+]} \text{ or } \boxed{\text{pH} = -\log [\text{H}_3\text{O}^+]}$$

$$\boxed{\text{pH} = \log \frac{1}{[\text{H}^+]}} \quad \text{pOH} = -\log [\text{OH}^-]$$

$$\boxed{\text{pH} + \text{pOH} = 14} \quad \text{and} \quad \boxed{\text{pH} + \text{pOH} = \text{p}K_w}$$

$$\boxed{\text{p}K_a + \text{p}K_b = \text{p}K_w}$$

## Salt Hydrolysis

- ◆ **Buffer solutions :** Buffer solution is defined as a solution which resists the change in its pH value when small amount of acid or base is added to it or when the solution is diluted. Buffer solution has a definite pH value at specific temperature and it does not change on keeping for a long time.

Buffers are classified into two categories :

- ◆ **Simple buffers :** These are the solutions of salt of weak acid and weak base. For example,  $\text{CH}_3\text{COONH}_4$  (ammonium acetate).
- ◆ **Mixed buffers :** These are the mixture of two solutions. These are further of two types :
  - **Acidic buffers :** These are the solutions of a mixture of weak acid and salt of this weak acid with strong base. For example,  $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$ . They have pH value lesser than 7.
  - **Basic buffers :** These are the solutions of mixture of a weak base and salt of this weak base with strong acid. For example,  $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$ . They have the pH value more than 7.



# NEET

## ONLINE TEST SERIES

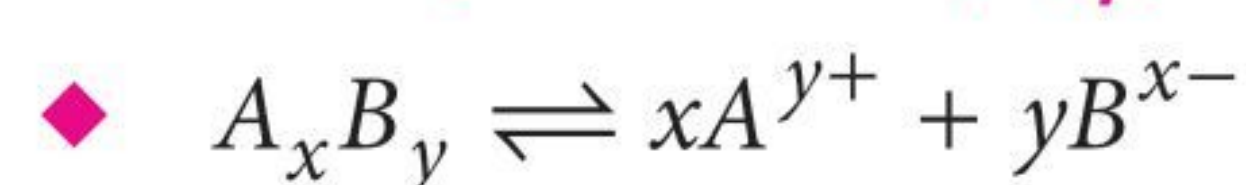
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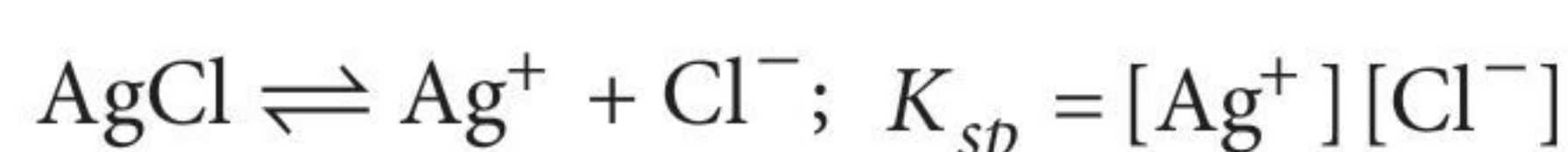


## Solubility Product ( $K_{sp}$ )



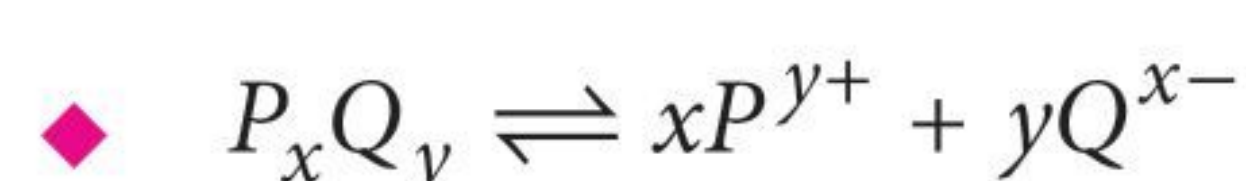
Solubility product ( $K_{sp}$ ) =  $[A^{y+}]^x [B^{x-}]^y$

For example,

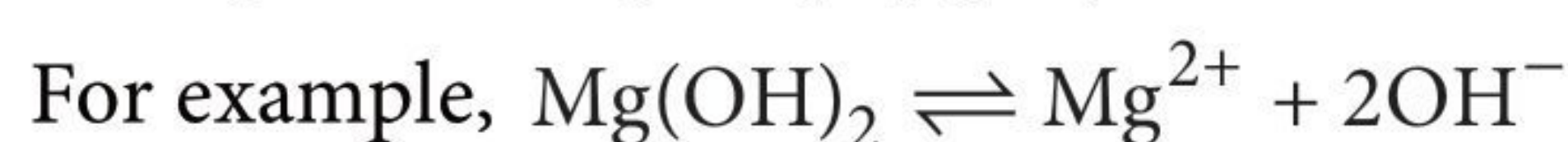


Salt type	Relation between $K_{sp}$ and $S$	Examples
$AB_2$	$K_{sp} = (S)(2S)^2 = 4S^3$	$PbCl_2$ , $HgCl_2$
$A_2B$	$K_{sp} = (2S)^2(S) = 4S^3$	$Ag_2CrO_4$ , $Ag_2C_2O_4$ , $Ag_2SO_4$
$AB_3$	$K_{sp} = (S)(3S)^3 = 27S^4$	$Fe(OH)_3$ , $Al(OH)_3$ , $Cr(OH)_3$
$A_3B_2$	$K_{sp} = (3S)^3(2S)^2 = 108S^5$	$Ca_3(PO_4)_2$ , $Zn_3(PO_4)_2$
$AB$	$K_{sp} = (S)(S) = S^2$	$AlPO_4$ , $AgCl$ , $AgBr$ , $PbSO_4$ , $BaSO_4$ , $ZnS$

## Ionic Product



Ionic product =  $[P^{y+}]^x [Q^{x-}]^y$



Ionic product =  $[Mg^{2+}][OH^-]^2$

If solubility product > Ionic Product (Solution is unsaturated)

If solubility product < Ionic Product (ppt. will be formed)

If solubility product = Ionic Product (Saturated solution)

## Common Ion Effect

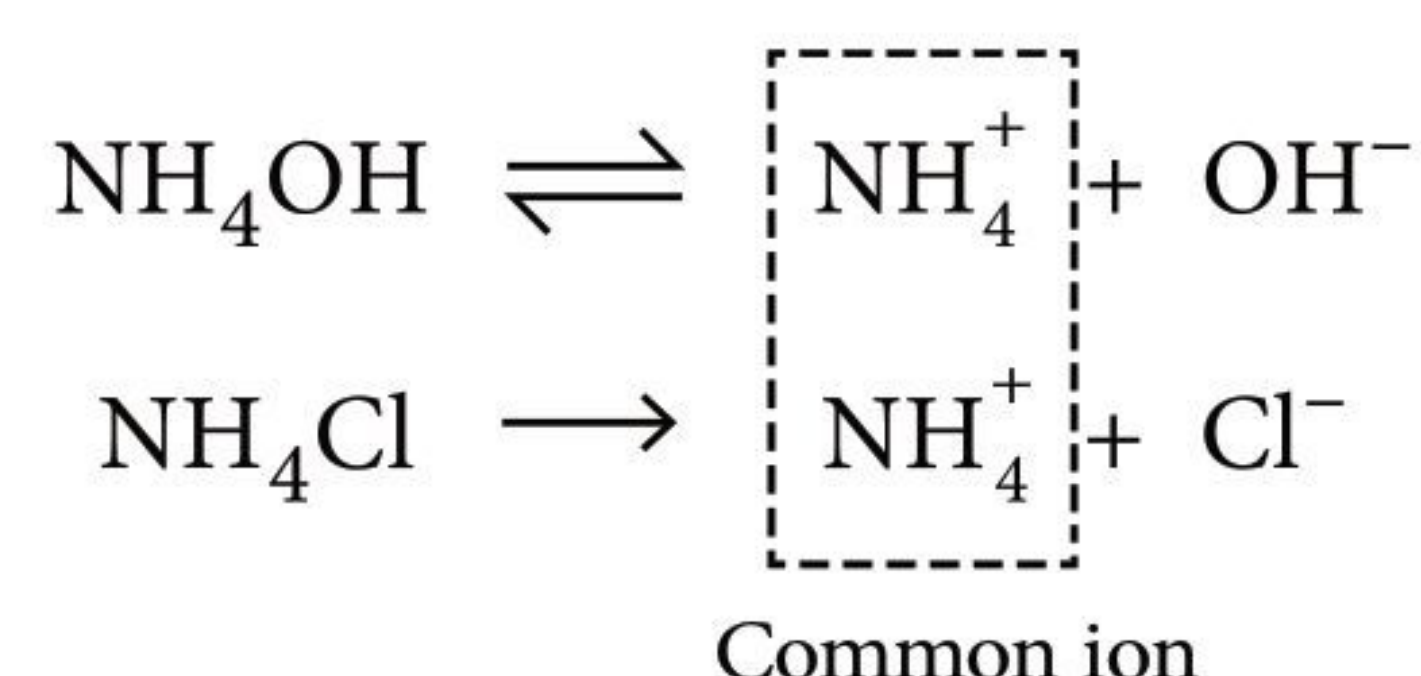
◆ Common ion effect is defined as, the suppression of ionization of weak electrolytes by addition of strong electrolytes having an ion common to weak electrolyte.

For example, weak base  $NH_4OH$  ionizes to a small extent.



When a strong electrolyte like  $NH_4Cl$  or  $NaOH$  is added to this solution, a common ion  $NH_4^+$  and

$OH^-$  respectively is furnished so that the equilibrium is shifted to the right, according to Le-Chatelier's principle, ionization of  $NH_4OH$  is suppressed.



Thus, degree of dissociation of an electrolyte decreases by common ion effect but dissociation constant of that electrolyte remains constant.

## Questions for Practice

- Equilibrium constant for a reaction is 100. What will be the equilibrium constant for the reverse reaction? (NCT 2017)
- At a certain temperature and total pressure of  $10^5$  Pa, iodine vapour contains 40% by volume of I atoms :  $I_{2(g)} \rightleftharpoons 2I_{(g)}$  Calculate  $K_p$  for the equilibrium. (NCERT, NCT 2014, 2015)
- Dihydrogen gas is obtained from natural gas by partial oxidation with steam as per following endothermic reaction,  $CH_{4(g)} + H_{2O(g)} \rightleftharpoons CO_{(g)} + 3H_{2(g)}$  How will the values of  $K_p$  and composition of equilibrium mixture be affected by :  
(i) increasing the pressure  
(ii) increasing the temperature  
(iii) using a catalyst? (NCERT, NCT 2017)
- Calculate the pH at 0.1M solution of acetic acid if the degree of dissociation of acid is 0.0132. (KVS 2017)
- Calculate the solubility of  $A_2X_3$  in pure water, assuming that neither kind of ion reacts with water. The solubility product of  $A_2X_3$ ,  $K_{sp} = 1.1 \times 10^{-23}$ . (NCERT, NCT 2017)

## MONTHLY TEST DRIVE CLASS XI ANSWER KEY

- |               |            |            |           |            |
|---------------|------------|------------|-----------|------------|
| 1. (b)        | 2. (c)     | 3. (d)     | 4. (b)    | 5. (b)     |
| 6. (d)        | 7. (b)     | 8. (b)     | 9. (c)    | 10. (b)    |
| 11. (d)       | 12. (d)    | 13. (d)    | 14. (c)   | 15. (a)    |
| 16. (d)       | 17. (b)    | 18. (b)    | 19. (a)   | 20. (a, d) |
| 21. (a, c, d) | 22. (a, c) | 23. (b, c) | 24. (1.8) | 25. (7)    |
| 26. (7.5)     | 27. (b)    | 28. (d)    | 29. (b)   | 30. (b)    |



## Solutions

1. Mathematically, Charles' law can be represented as  $V_t = V_0 + \frac{V_0}{273} \times t = V_0 \left( 1 + \frac{t}{273} \right)$ , where  $V_t$  is the volume of the gas at any temperature and  $V_0$  is its volume at  $0^\circ\text{C}$ . From the above relation, it is clear that at  $-273^\circ\text{C}$ ,  $V_t$  will be zero and below this temperature, the volume will be negative, which is meaningless. Hence,  $-273^\circ\text{C}$  is the lowest temperature of a gas.

2.  $PV = nRT$

$$\text{or } P = \frac{wRT}{MV} \quad \left( \text{Since } n = \frac{w}{M} \right)$$

$$\text{or } P = \frac{dRT}{M} \quad \left[ \text{Since } d = \frac{w}{V} \right]$$

$$\text{or, } P \propto d$$

Hence, density ( $d$ ) of a gas  $\propto P$ , because  $R$ ,  $T$  and  $M$  are constants.

3. Moles of oxygen  $= \frac{8}{32} = 0.25$

$$\text{Moles of hydrogen} = \frac{4}{2} = 2$$

$$\text{Total number of moles} = 2.25$$

$$V = 1 \text{ dm}^3, T = 300 \text{ K},$$

$$R = 0.083 \text{ bar dm}^3 \text{ K}^{-1} \text{ mol}^{-1}$$

$$PV = nRT$$

$$P = \frac{2.25 \times 0.083 \times 300}{1} = 56.025 \text{ bar}$$

4. van der Waals' equation for one mole of a gas is :

$$\left( P + \frac{a}{V^2} \right) (V - b) = RT$$

where  $P$  = Pressure,  $T$  = Temperature,  $V$  = Volume,  $R$  = Gas constant, ' $a$ ' and ' $b$ ' are van der Waals' constants.

5. Heat absorbed by the system ( $q$ ) = 701 J  
Work done by the system ( $w$ ) = -394 J  
According to first law of thermodynamics,  
 $\Delta U = q + w = 701 + (-394) = 701 - 394 = 307 \text{ J}$
6. **Intensive properties:** Temperature, Molar heat capacity.
7. (a) **Extensive properties:** Properties that depend on the quantity of matter contained in the system, e.g., mass, volume, etc.  
**Intensive properties:** Properties which depend on the nature of the substance and not on the amount

of substance, e.g., viscosity, etc.

$$(b) \Delta H = 41 \text{ kJ/mole}, R = 8.3 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1},$$

$$\Delta n_g = 1 \text{ mole}, T = 100 + 273 = 373 \text{ K}$$

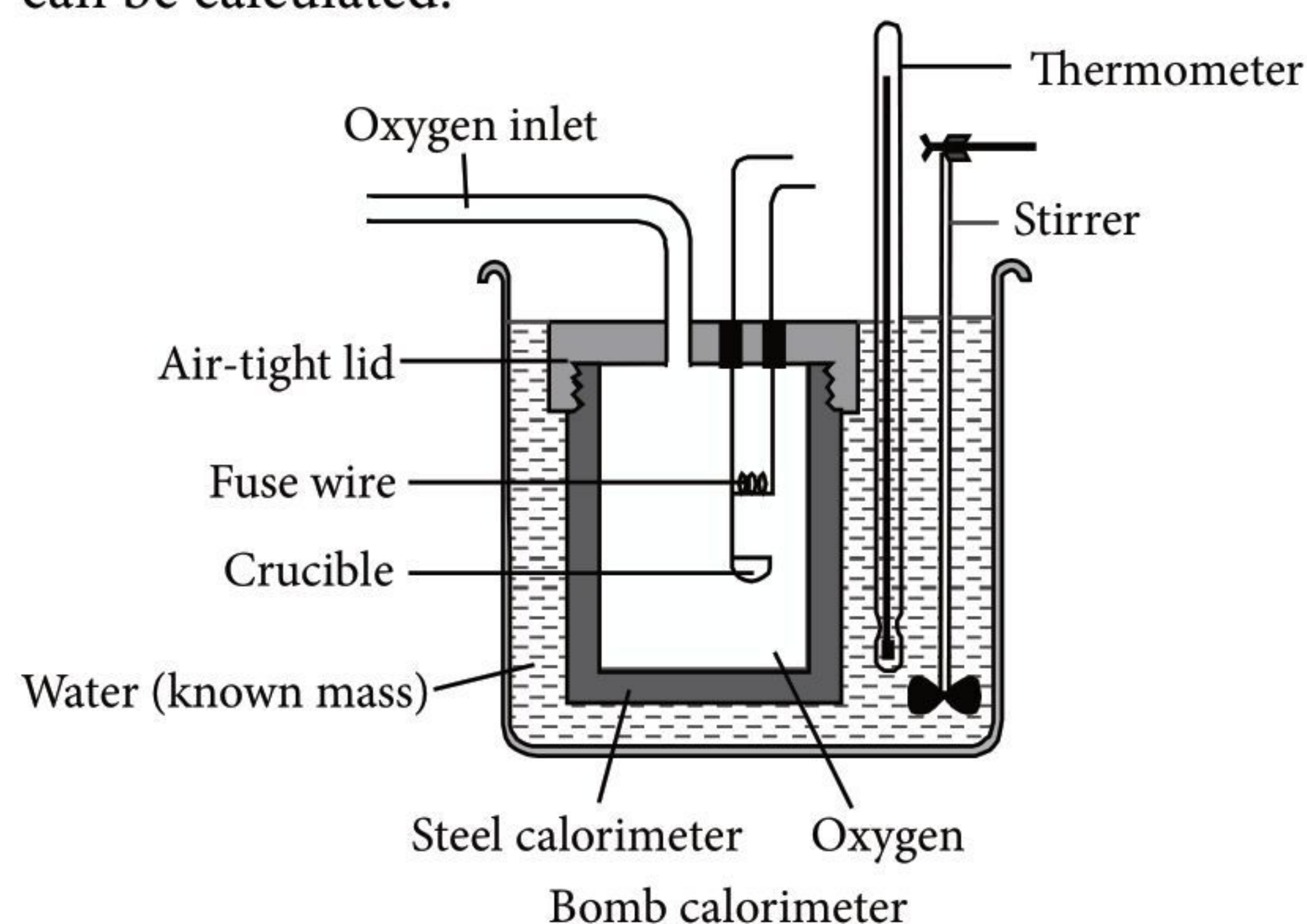
$$\Delta H = \Delta E + \Delta n_g RT$$

$$\Delta E = \Delta H - \Delta n_g RT$$

$$\Delta E = 41 - 1 \times 373 \times 8.3 \times 10^{-3} \\ = 41 - 3.096 = 37.904 \text{ kJ}$$

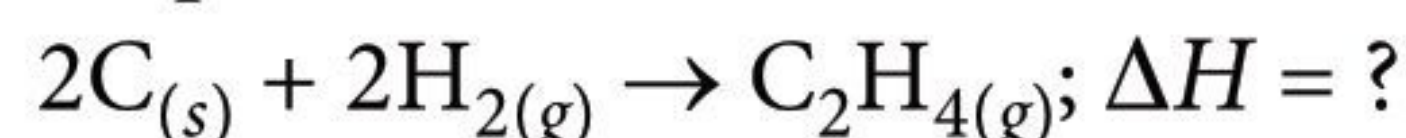
8. (a) Bomb calorimeter

(b) A bomb calorimeter is used to measure the internal energy change ( $\Delta U$ ) when one mole of a substance is completely burnt in oxygen using an apparatus called bomb calorimeter. A known amount of the substance is placed in the crucible, oxygen is passed at 20 atm pressure and then the substance is ignited using the heated wire. Combustion of the substance takes place. The rise in water, temperature is measured and from this the heat capacity of apparatus can be calculated.



9. (a)  $\text{C}_{(s)} + \text{O}_{2(g)} \rightarrow \text{CO}_{2(g)}; \Delta_f H^\circ = -393.5 \text{ kJ/mol} \dots(i)$   
 $\text{H}_{2(g)} + 1/2 \text{O}_{2(g)} \rightarrow \text{H}_2\text{O}_{(l)}; \Delta_f H^\circ = -249 \text{ kJ/mol} \dots(ii)$   
 $\text{C}_2\text{H}_{4(g)} + 3\text{O}_{2(g)} \rightarrow 2\text{CO}_{2(g)} + 2\text{H}_2\text{O}_{(g)}; \Delta H = -1323 \text{ kJ} \dots(iii)$

Required reaction is :



On applying,  $2 \times \text{eq (i)} + 2 \times \text{eq (ii)} - \text{eq (iii)}$ , we get

$$\Delta_f H_{\text{C}_2\text{H}_4} = 2 \times -393.5 + 2 \times (-249) - (-1323) \\ = -787 - 498 + 1323 = 38 \text{ kJ/mol}$$

(b) According to this law, the standard enthalpy of reaction is the algebraic sum of the standard enthalpies of reaction into which the overall reaction may be divided at constant temperature.

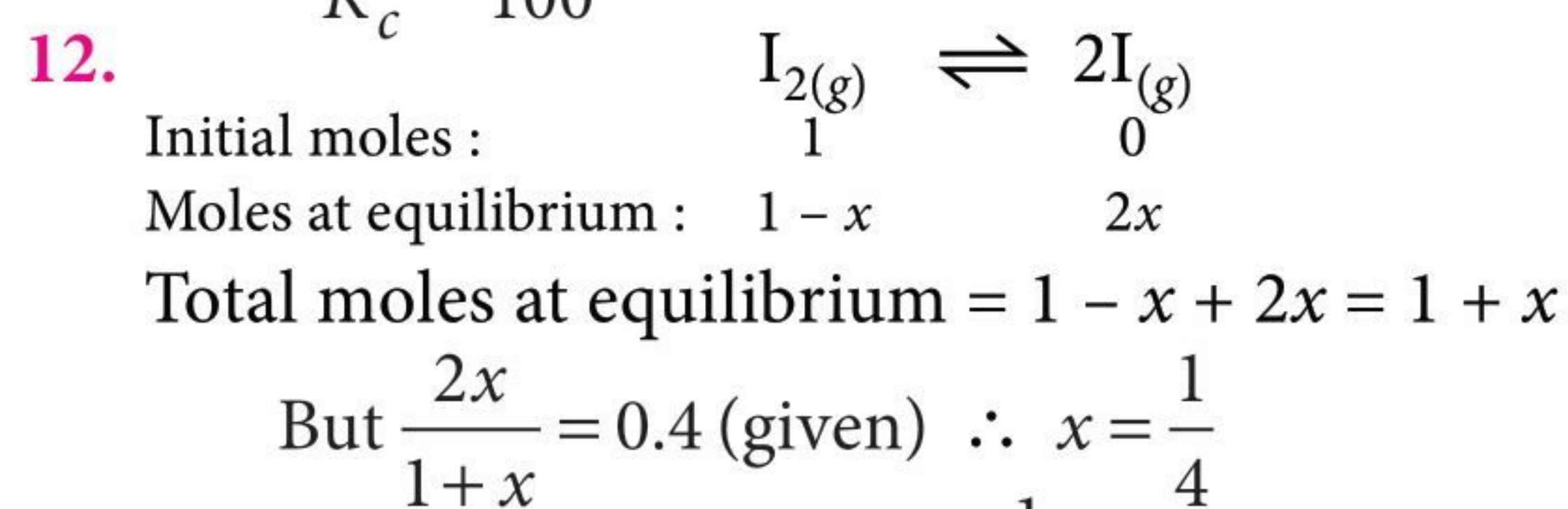
10.  $\Delta G^\circ = -2.303 RT \log K$

$$\Delta G^\circ = 0$$

$$\log K = 0 \text{ or, } K = 1$$



$$11. K'_c = \frac{1}{K_c} = \frac{1}{100} = 0.01$$



So, mole fraction of  $\text{I}_2 = \frac{1-\frac{1}{4}}{1+\frac{1}{4}} = \frac{3}{5} = 0.6$ ,

mole fraction of  $\text{I} = \frac{2 \times \frac{1}{4}}{1+\frac{1}{4}} = \frac{2}{5} = 0.4$

$p_{\text{I}} = 0.4 \times 10^5 \text{ Pa}$  or  $p_{\text{I}_2} = 0.6 \times 10^5 \text{ Pa}$

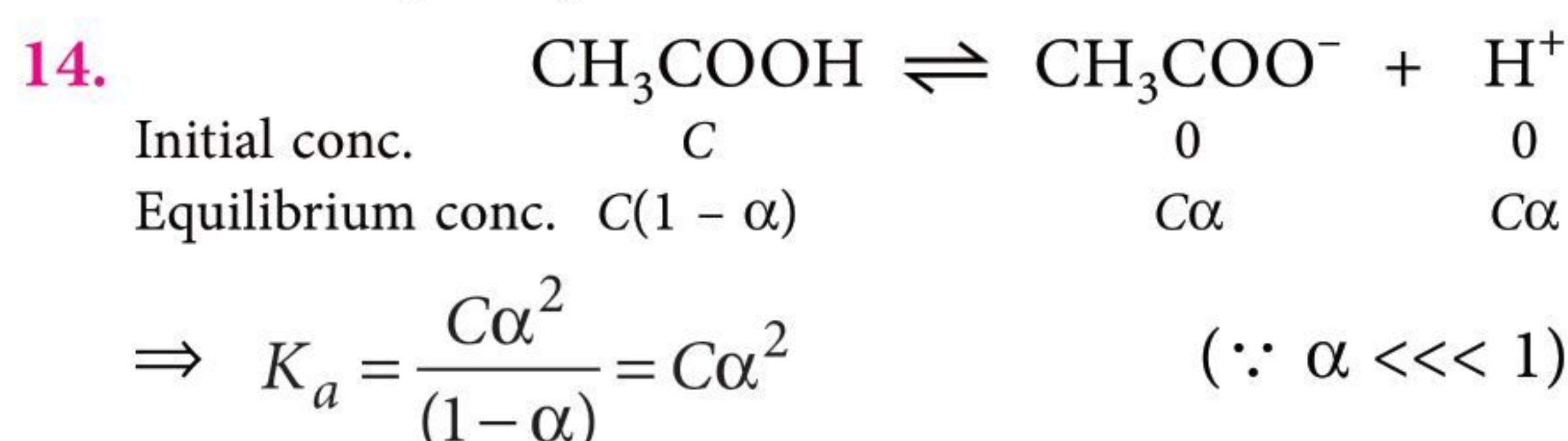
$$K_p = \frac{p_{\text{I}}^2}{p_{\text{I}_2}} = \frac{(0.4)^2 (10^5)^2}{(0.6)(10^5)} = 2.67 \times 10^4$$

13. 
$$K_p = \frac{p_{\text{CO}} \times p_{\text{H}_2}^3}{p_{\text{CH}_4} \times p_{\text{H}_2\text{O}}}$$

(i) By Le-Chatelier's principle, on increasing the pressure, equilibrium will shift in the backward direction where number of moles decreases.

(ii) As the given reaction is endothermic, by Le-Chatelier's principle, equilibrium will shift in the forward direction with increase in temperature.

(iii) Equilibrium composition will not be disturbed by the presence of catalyst but equilibrium will be attained quickly.



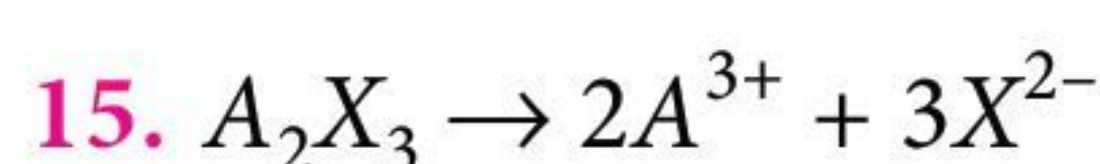
$$= 0.1 \times (0.0132)^2 = 1.74 \times 10^{-5}$$

$$\Rightarrow [\text{H}^+] = C\alpha = 0.1 \times 0.0132$$

$$= 1.32 \times 10^{-3} \text{ M}$$

$$\Rightarrow \text{pH} = -\log[\text{H}^+] = -\log(1.32 \times 10^{-3})$$

$$= 3 - 0.1206 \approx 2.88$$



$$K_{sp} = [\text{A}^{3+}]^2 [\text{X}^{2-}]^3 = 1.1 \times 10^{-23}$$

If  $s$  = solubility of  $\text{A}_2\text{X}_3$ , then  $[\text{A}^{3+}] = 2s$ ;  $[\text{X}^{2-}] = 3s$

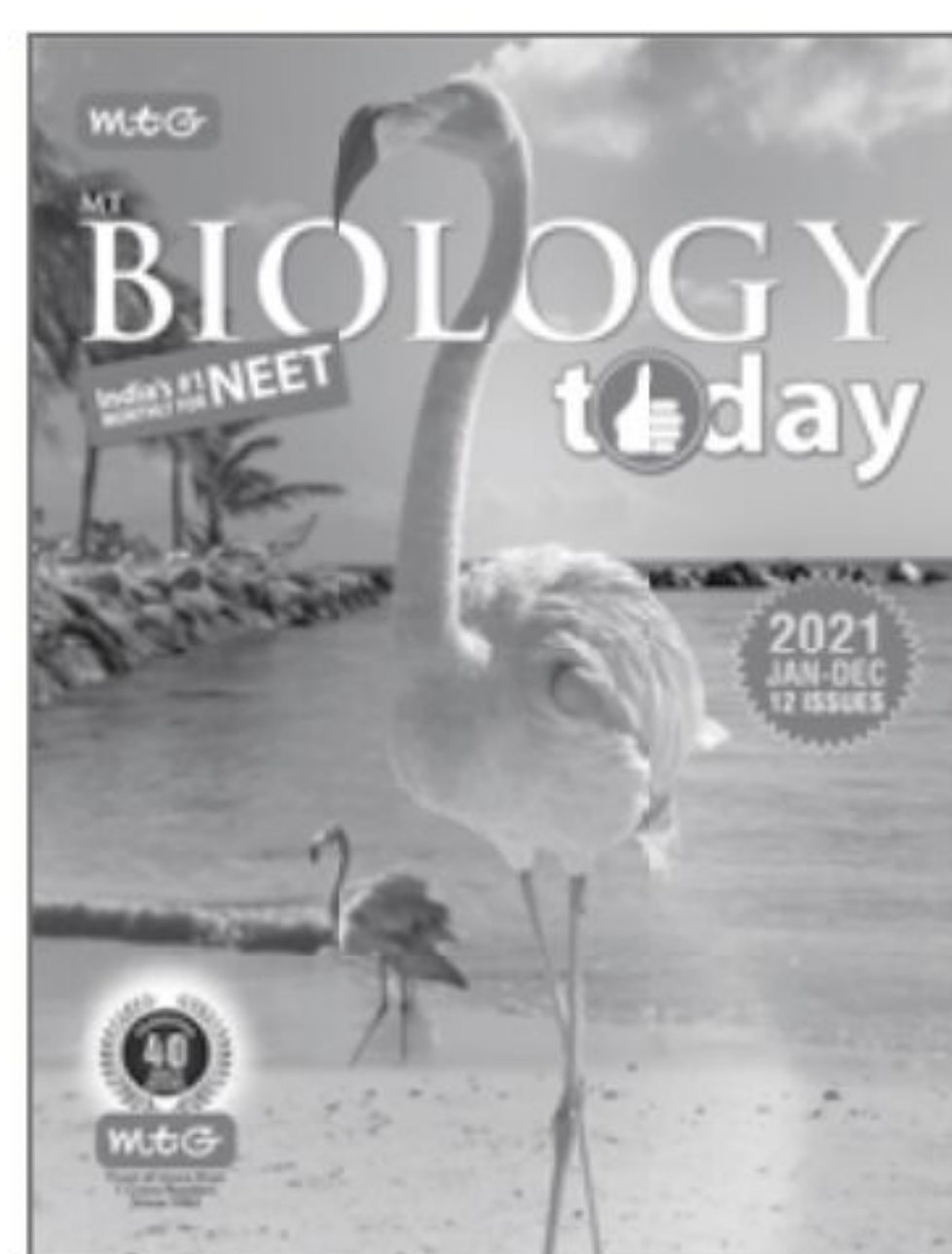
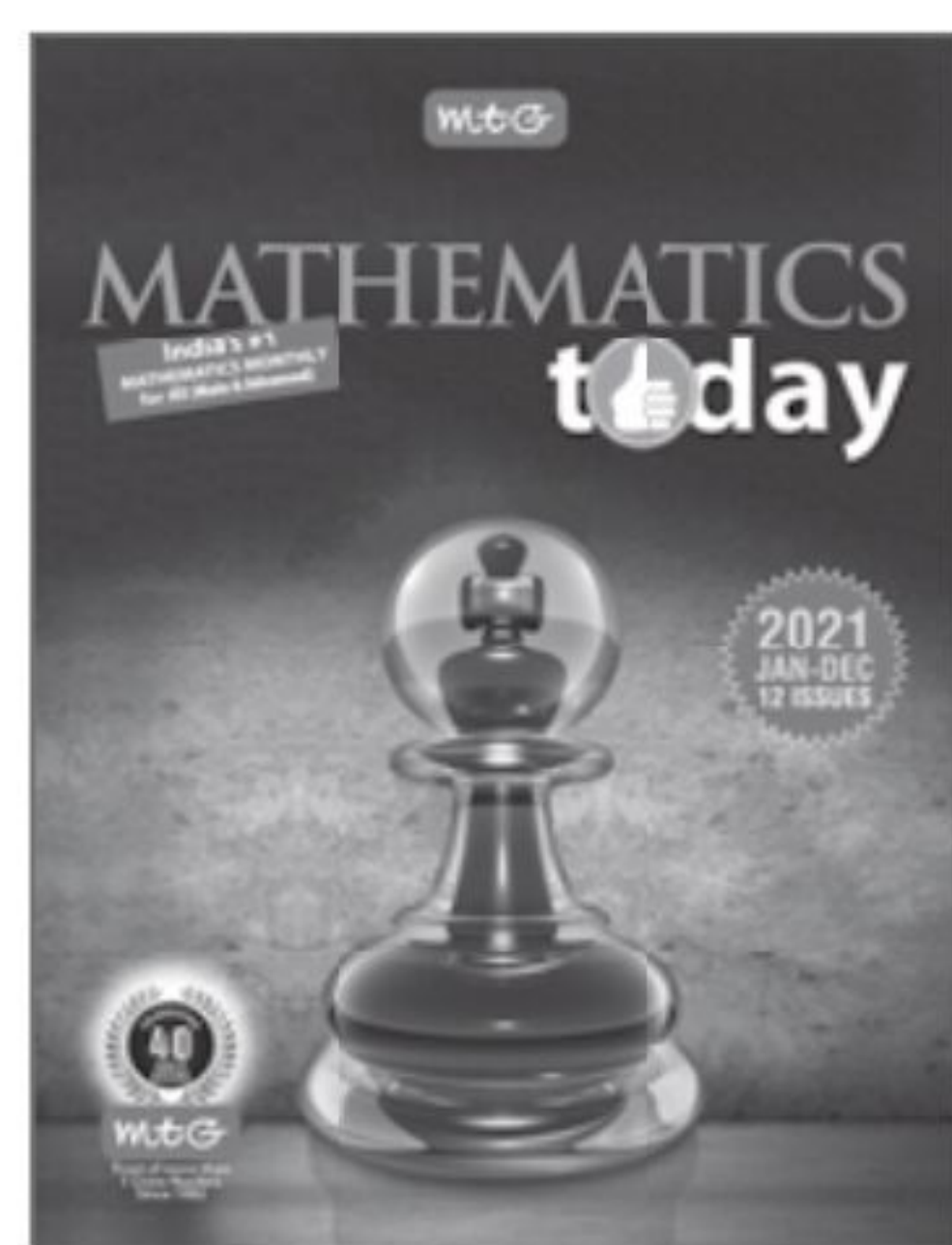
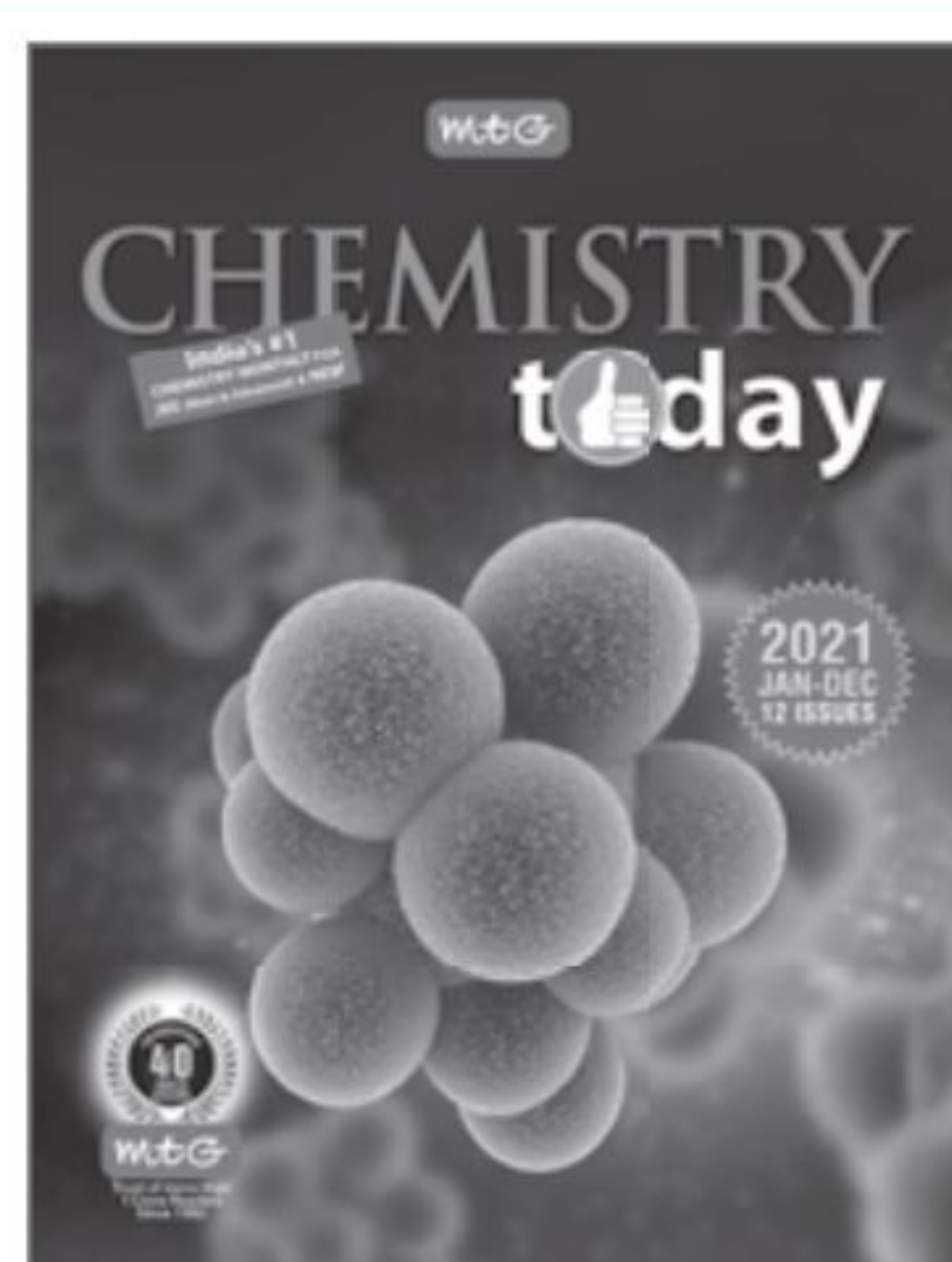
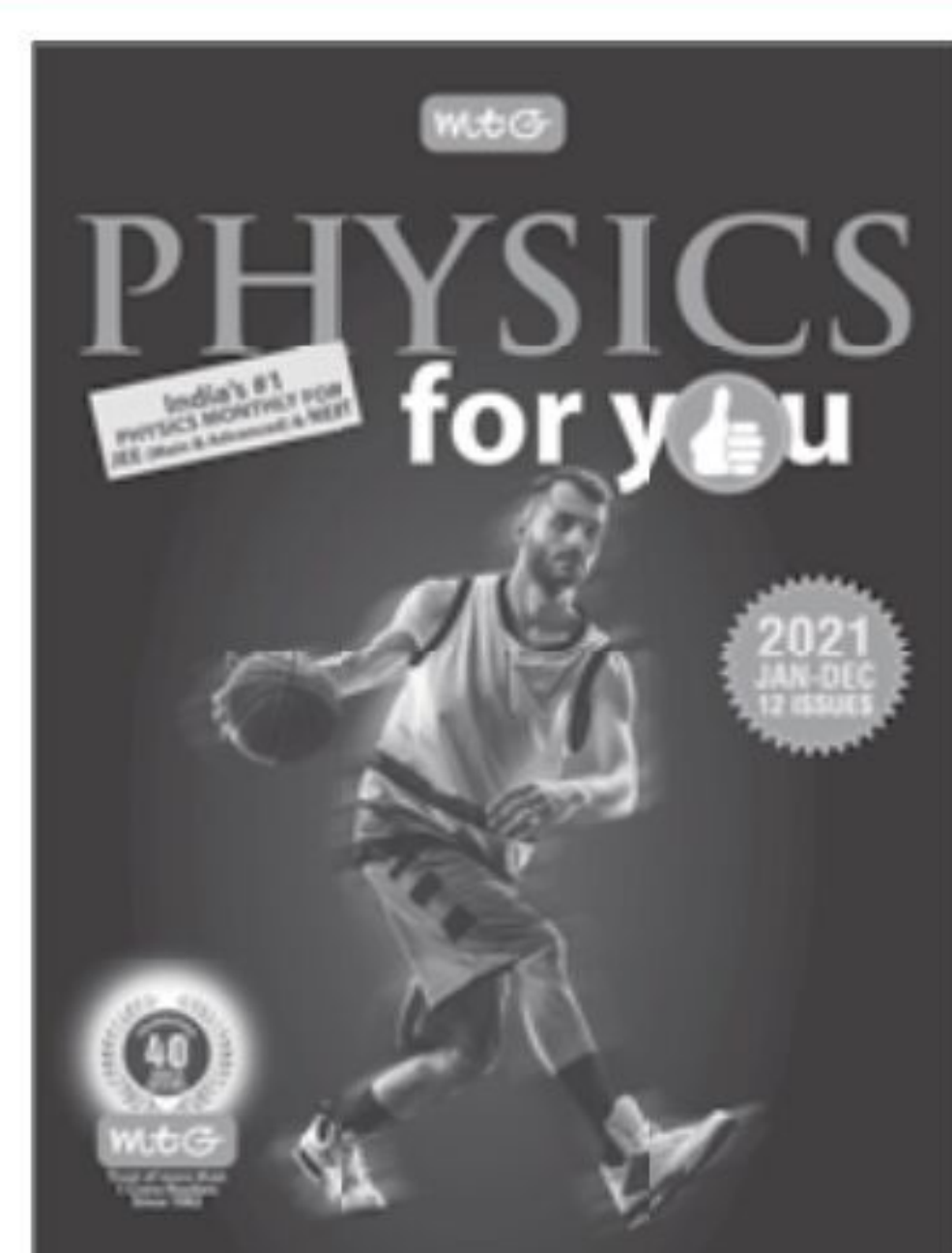
Therefore,  $K_{sp} = (2s)^2(3s)^3 = 108s^5 = 1.1 \times 10^{-23}$

Thus,  $s^5 = 1 \times 10^{-25}$

$\therefore s = 1.0 \times 10^{-5} \text{ mol/L}$



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# CBSE

## warm-up!

Term-II

CLASS - XI

### Practice Paper 2022

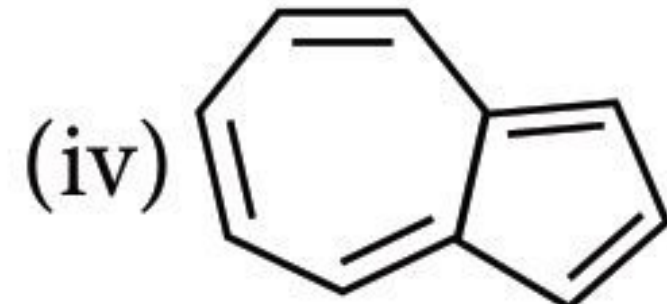
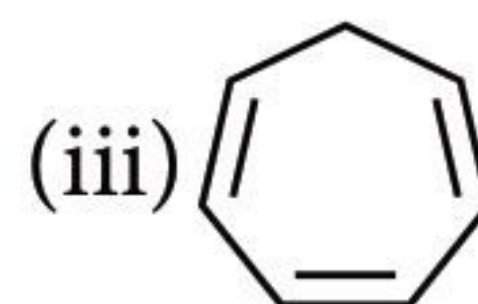
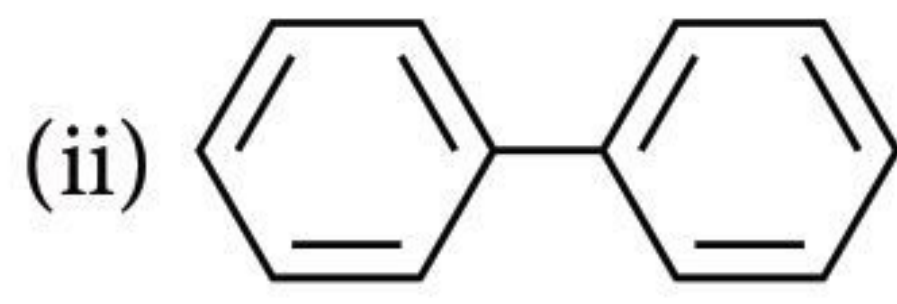
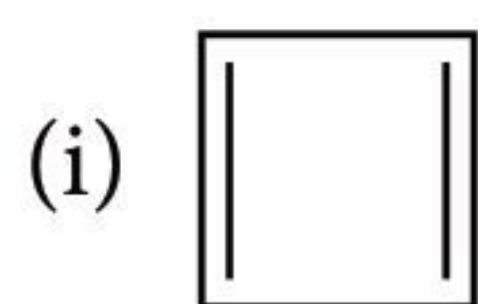
Time Allowed : 2 hours  
Maximum Marks : 35

**General Instructions :** Read the following instructions carefully.

1. There are 12 questions in this question paper with internal choice.
2. SECTION A - Q. No. 1 to 3 are very short answer questions carrying 2 marks each.
3. SECTION B - Q. No. 4 to 11 are short answer questions carrying 3 marks each.
4. SECTION C - Q. No. 12 is case based question carrying 5 marks.
5. All questions are compulsory.
6. Use of log tables and calculators is not allowed.

#### SECTION - A

1. Why are superoxides of alkali metals paramagnetic, whereas normal oxides are diamagnetic?
2. Convert :  
(i) But-2-ene to ethanal  
(ii) Propene to propan-2-ol.
3. Predict which of the following systems would be aromatic and why?



#### SECTION - B

4. On the basis of their interaction energy and thermal energy explain why  
(i) a solid has high rigidity?  
(ii) in gas, molecules are sufficiently apart from one another?  
(iii) liquid has no definite shape?

OR

- A 5 L vessel contains 1.4 g of nitrogen. When heated to 1800 K, 30% of molecules are dissociated into atoms. Calculate the pressure of the gas at 1800 K.
5. What is the state of hybridisation of carbon in  
(a)  $\text{CO}_3^{2-}$  (b) diamond (c) graphite?
  6. Determine the value of  $\Delta H$  and  $\Delta U$  for the reversible isothermal evaporation of 90.0 g of water at  $100^\circ\text{C}$ . Assume that water vapour behaves as an ideal gas and heat of evaporation of water is  $540 \text{ cal g}^{-1}$ . ( $R = 2.0 \text{ cal mol}^{-1} \text{ K}^{-1}$ )

OR

- (i) State Hess's law of constant heat summation.  
(ii) The standard enthalpy of combustion at  $25^\circ\text{C}$  of  $\text{H}_2$ ,  $\text{C}_6\text{H}_{10}$  and cyclohexane ( $\text{C}_6\text{H}_{12}$ ) are  $-241$ ,  $-3800$ ,  $-3920 \text{ kJ mol}^{-1}$  respectively. Calculate the heat of hydrogenation of cyclohexene ( $\text{C}_6\text{H}_{10}$ ).
7. (i)  $\text{LiF}$  is insoluble in water. Explain.  
(ii) Why does Li give red colour to the flame?  
(iii)  $\text{CO}_2$  does not burn in air and does not support



combustion, but a burning Mg wire continues to burn in it. Explain.

OR

- (i) The crystalline salts of alkaline earth metals contain more water of crystallisation than the corresponding alkali metal salts. Why?
  - (ii) Arrange the following sulphates of alkaline earth metals in order of decreasing thermal stability:  $\text{BeSO}_4$ ,  $\text{MgSO}_4$ ,  $\text{CaSO}_4$ ,  $\text{SrSO}_4$
  - (iii) Be and Mg do not impart colour to the flame like other alkaline earth metals. Give reason.
8.  $K_p = 0.04$  atm at 899 K for the equilibrium shown below. What is the equilibrium concentration of  $\text{C}_2\text{H}_6$  when it is placed in a flask at 4.0 atm pressure and allowed to come to equilibrium?
- $$\text{C}_2\text{H}_{6(g)} \rightleftharpoons \text{C}_2\text{H}_{4(g)} + \text{H}_{2(g)}$$
9. (i) Why trihalides of group 13 elements behave as Lewis acids ?
- (ii) Why aluminium chloride forms a dimer?
- (iii) Graphite is a conductor but diamond is not. Explain ?
10. Equal volumes of 0.002 M solutions of sodium iodate and copper chlorate are mixed together. Will it lead to precipitation of copper iodate? (For copper iodate,  $K_{sp} = 7.4 \times 10^{-8}$ )

OR

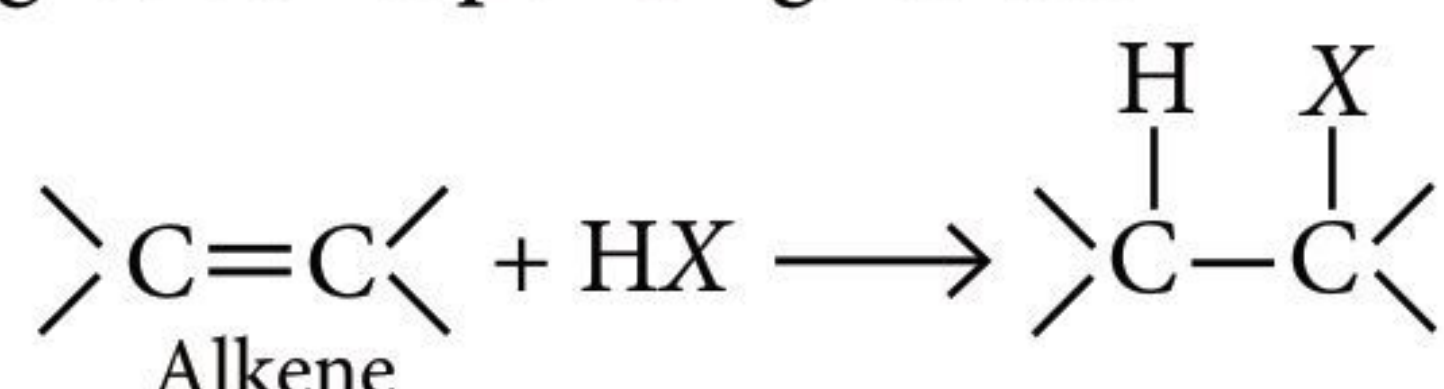
The degree of ionisation of 0.1 M bromoacetic acid solution is 0.132. Calculate pH of solution and  $pK_a$  of bromoacetic acid.

11. Answer the following :
- (i) What is compressibility factor  $Z$ ?
  - (ii) What is the value of  $Z$  for an ideal and non-ideal gas?
  - (iii) The compressibility factor  $Z$  for a gas is less than one. What does it signify?

### SECTION - C

12. Read the passage given below and answer the questions that follow:

Alkene reacts with hydrogen halides or halogen acids to give corresponding halides



In case of symmetrical alkenes having same groups on either side of double bond only one possible product is obtained.

In case of unsymmetrical alkenes having different groups on either side of the double bond, two theoretically possible products are obtained. The relative amount of two possible products is explained by Markovnikov's rule. But in presence of peroxide the product formed are contrary to Markovnikov's rule.

- (a) What do you understand by the Markovnikov's rule?
- (b) Complete the following reaction :  

$$\text{CH}_3 - \text{CH} = \text{CH}_2 + \text{HBr} \xrightarrow{\text{Organic peroxide}}$$
- (c) Complete the following reaction :  

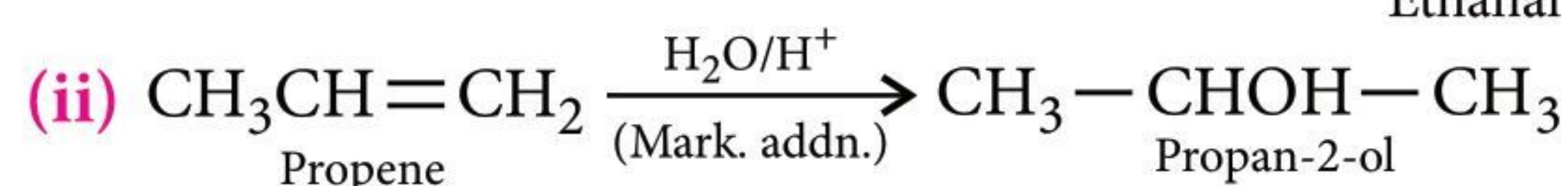
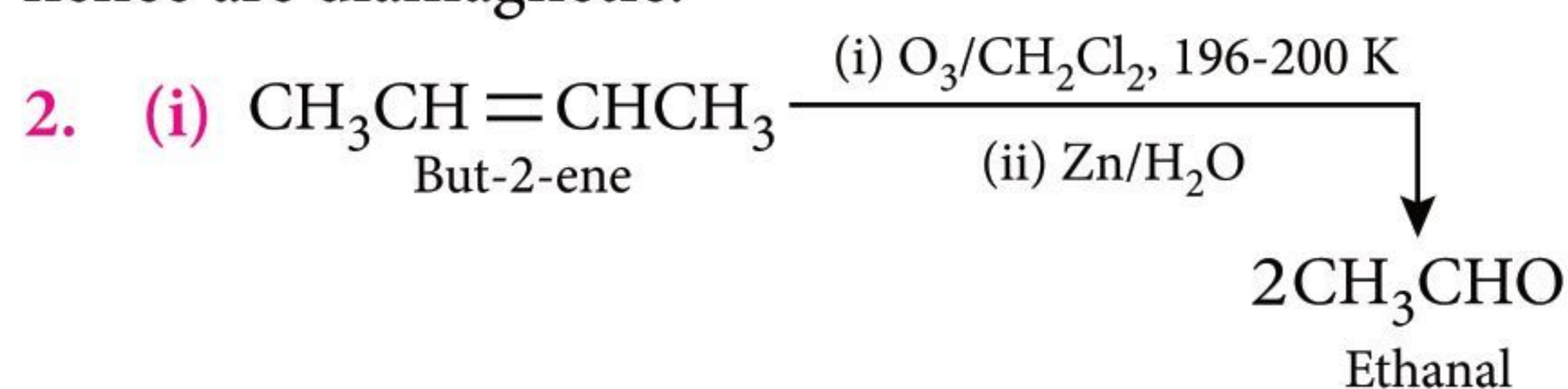
$$\text{CH}_3 - \text{CH} = \text{CH}_2 + \text{HBr} \longrightarrow$$
- (d) The intermediate carbocation formed in the reactions of HI, HBr and HCl with propene is the same and the bond energy of HCl, HBr and HI is  $430.5 \text{ kJ mol}^{-1}$ ,  $363.7 \text{ kJ mol}^{-1}$  and  $296.8 \text{ kJ mol}^{-1}$  respectively. What will be the order of reactivity of these halogen acids?

OR

Give mechanism of addition of HBr to propene.

### SOLUTIONS

1. Superoxides contain the ion ( $\text{O}_2^-$ ) which has the structure  $(:\ddot{\text{O}} \cdots \ddot{\text{O}}:)^-$  containing a three-electron bond, that is, they have one unpaired electron and hence they are paramagnetic. Normal oxides containing the ion  $\text{O}^{2-}$ , which do not have any unpaired electron and hence are diamagnetic.



3. Structures (ii) and (iv) are aromatic because they obey Huckel's rule. Others are not aromatic because (i) contains  $4\pi$  electrons and although (iii) contains  $6\pi$  electrons but it is not a conjugated system due to the presence of a  $sp^3$ -hybridised carbon.
4. (i) A solid has high rigidity because thermal motion is too weak to overcome the strong intermolecular forces of attraction.
- (ii) In a gas, thermal energy is so high that the molecules cannot come close together. Hence, there are large empty spaces between them.
- (iii) In a liquid, there is a reasonable balance between the attractive intermolecular forces and thermal energy.



Hence, molecules in a liquid exist together, *i.e.*, it is a condensed state of matter but there is no rigidity. That is why they have no definite shape.

OR

	$\text{N}_2$	$\rightleftharpoons$	$2\text{N}$
Initial moles	$\frac{1.4}{28} = 0.05$		0
Moles after dissociation	$0.05 - \frac{30}{100} \times 0.05 = 0.035$		$2 \times 0.015 = 0.030$

$\therefore$  Total number of moles =  $0.035 + 0.030 = 0.065$ ,  
*i.e.*,  $n = 0.065$  mol,  $V = 5$  L,  $T = 1800$  K,  $P = ?$

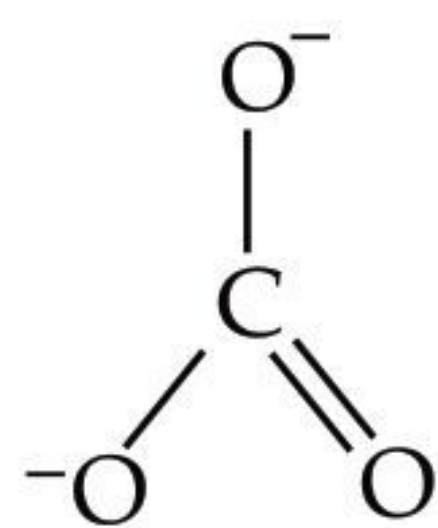
From  $PV = nRT$ , we get

$$P = \frac{nRT}{V}$$

$$= \frac{0.065 \text{ mol} \times 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 1800 \text{ K}}{5 \text{ L}}$$

$$= 1.92 \text{ atm}$$

5. (a) C in  $\text{CO}_3^{2-}$  ion is  $sp^2$  hybridised. This can be explained as :



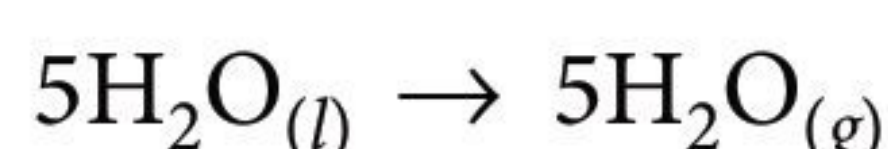
(b) Diamond : C is  $sp^3$  hybridised in diamond. This gives it a tetrahedral structure rendering it hard.

(c) Graphite : C is  $sp^2$  hybridised in graphite. It forms 3 bonds with 3 other carbon atoms in the same plane while the fourth covalency is satisfied by  $\pi$ -bonding. These  $\pi$ -electrons are delocalised over the whole sheet.

6. Heat of evaporation =  $540 \text{ cal g}^{-1}$

$\therefore \Delta H$  for 90 g water =  $540 \times 90 = 48600 \text{ cal}$

$$90 \text{ g H}_2\text{O} = \frac{90}{18} = 5 \text{ mol of H}_2\text{O}$$



$$\Delta n_g = 5 - 0 = 5$$

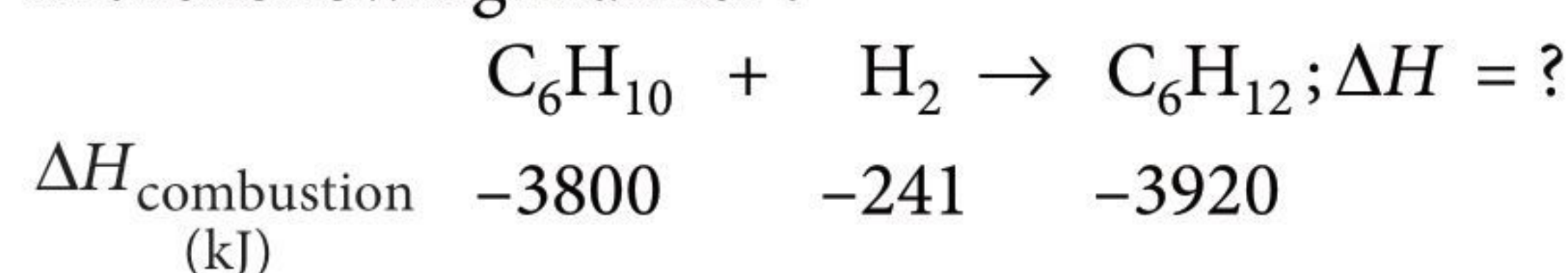
$$\Delta H = \Delta U + \Delta n_g RT \Rightarrow \Delta U = \Delta H - \Delta n_g RT$$

$$\Delta U = 48600 - 5 \times 2 \times 373 = 44870 \text{ cal} = 44.87 \text{ Kcal}$$

OR

(i) According to this law, the standard enthalpy of a reaction is the algebraic sum of the standard enthalpies of its intermediate reactions into which the overall reaction may be divided at constant temperature.

(ii) Hydrogenation of cyclohexene can be represented in the following manner :



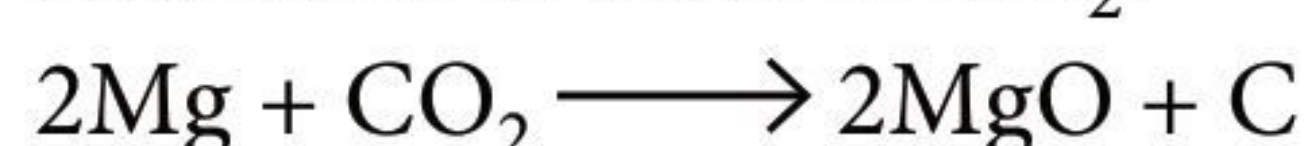
$$\Delta H_{\text{Reaction}} = \Delta H_{\text{C (Reactants)}} - \Delta H_{\text{C (Products)}}$$

$$= -3800 - 241 - (-3920) = -121 \text{ kJ mol}^{-1}$$

7. (i) The  $\text{Li}^+$  ion has highest hydration energy due to small size as compared to other alkali metals. But small  $\text{Li}^+$  and  $\text{F}^-$  interact strongly resulting in high lattice energy of  $\text{LiF}$ , which is responsible for its insolubility.

(ii) The reason for colouration in flame is due to the fact that even the small amount of energy of the flame causes the excitation of the outermost electron of the alkali metal atom and is raised to higher energy level. When the excited electron returns back to its original position (ground state), it releases the absorbed energy as visible light. The frequency of the light emitted in the Bunsen flame is minimum in case of lithium and corresponds to the red region of spectrum.

(iii) Burning magnesium reduces  $\text{CO}_2$  to C, hence it continues to burn in  $\text{CO}_2$ .



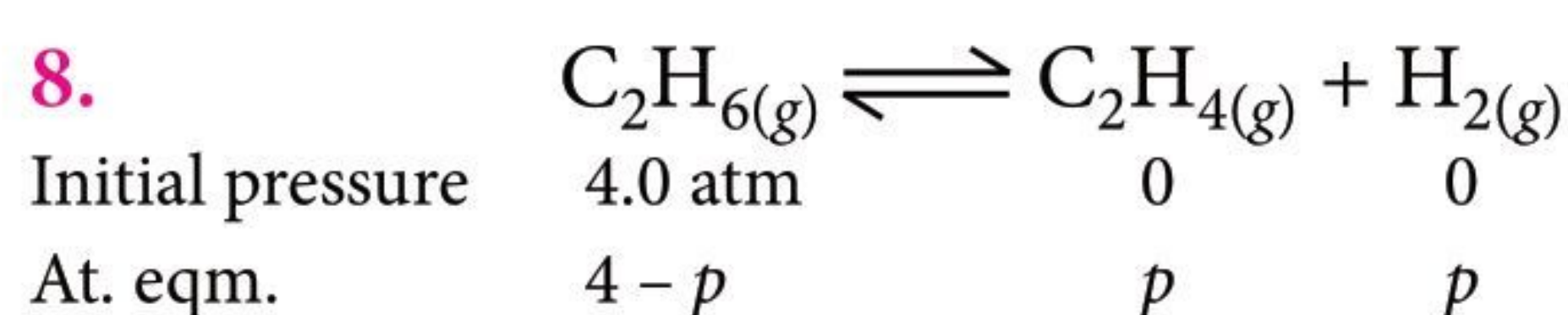
OR

(i) As the size of alkaline earth metal ions (group 2) is smaller as compared to those of alkali metal ions (group 1) so in crystalline form the salts of alkaline earth metals have more water molecules as compared to those of alkali metal salts.

(ii) Sulphates of alkaline earth metals decompose on heating to give oxides (MO).

The temperature of decomposition decreases with decreases in basic nature of the metal. Thus, the order of stability of alkaline earth metal sulphates is  $\text{SrSO}_4 > \text{CaSO}_4 > \text{MgSO}_4 > \text{BeSO}_4$ .

(iii) Due to high ionization enthalpy the electrons in Be and Mg are too strongly bound to get excited by the flame.



Applying law of chemical equilibrium,

$$K_p = \frac{p_{\text{C}_2\text{H}_4} \times p_{\text{H}_2}}{p_{\text{C}_2\text{H}_6}} \Rightarrow 0.04 = \frac{p^2}{4 - p}$$

$$\text{or, } p^2 = 0.16 - 0.04p \text{ or } p^2 + 0.04p - 0.16 = 0$$

$$\therefore p = \frac{-0.04 \pm \sqrt{0.0016 - 4(-0.16)}}{2} = \frac{-0.04 \pm 0.80}{2}$$

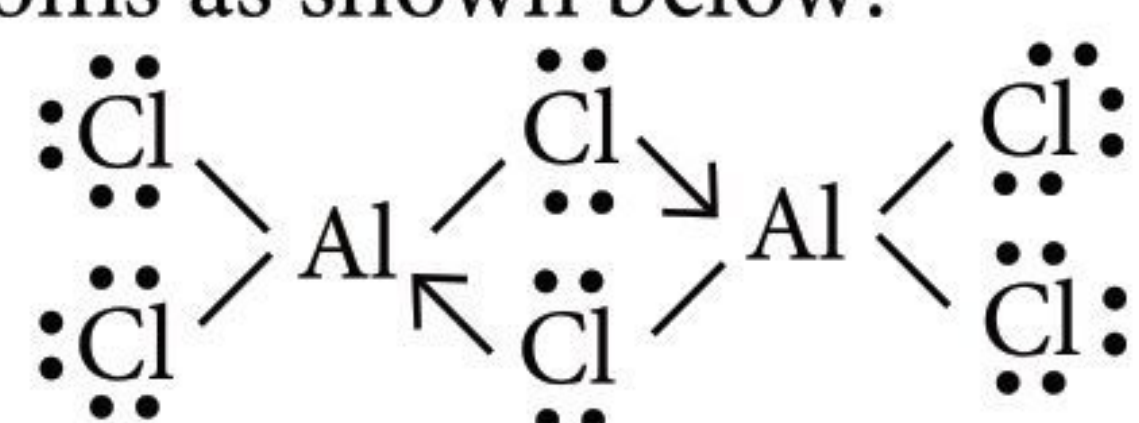
$$\text{Taking positive value, } p = \frac{0.76}{2} = 0.38$$

$$\therefore [\text{C}_2\text{H}_6]_{\text{eq}} = 4 - 0.38 \text{ atm} = 3.62 \text{ atm}$$



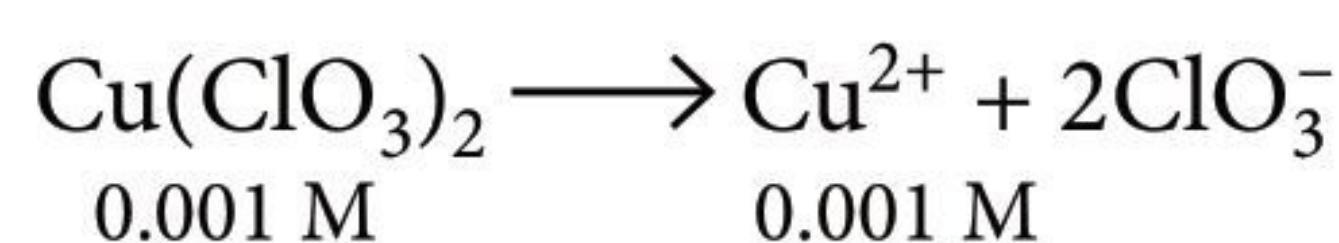
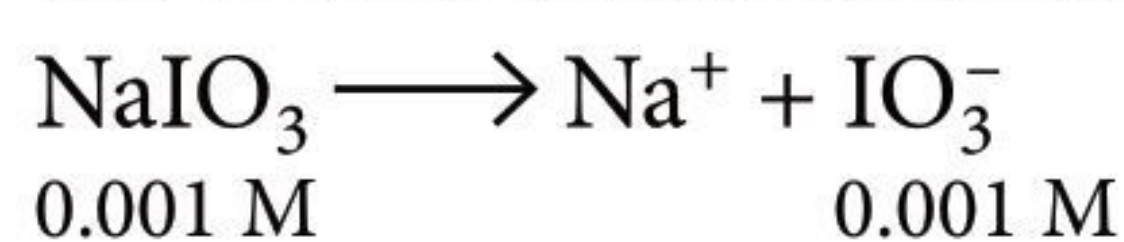
9. (i) The trihalides of group 13 elements have only six electrons around the central atom and hence, have a strong tendency to accept a pair of electrons to acquire the nearest inert gas configuration and thus behave as Lewis acids.

(ii) Aluminium atom in aluminium chloride contains 6 electrons around it. So it requires 2 more electrons to complete its octet. Since Al can accommodate four Cl atoms around it thus its octet is completed by dimerisation when chlorine donate lone pair to aluminium atoms as shown below:



(iii) Graphite has a layered structure in which each C atom is  $sp^2$  hybridised and makes Three sigma bonds with three neighbouring carbon atoms. Fourth electron forms a  $\pi$  bond and these  $\pi$  electrons are delocalised and conduct electricity. In diamond each C atom is  $sp^3$ -hybridised and no delocalised or mobile electrons are available.

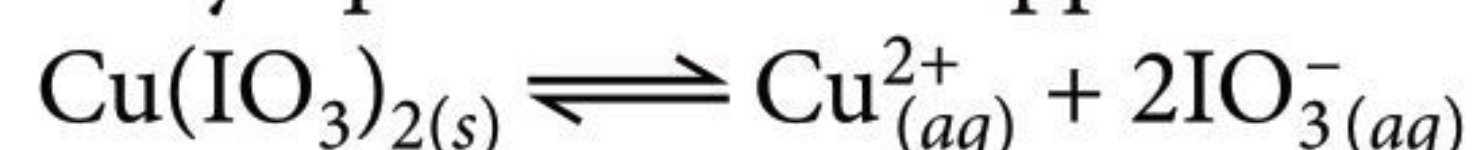
10. When equal volumes of sodium iodate and copper chlorate are mixed, the molar concentrations of both the solutes would be reduce to half i.e., 0.001 M.



$\therefore$  After mixing,  $[\text{IO}_3^-] = [\text{NaIO}_3] = 0.001 \text{ M}$

$[\text{Cu}^{2+}] = [\text{Cu}(\text{ClO}_3)_2] = 0.001 \text{ M}$

Solubility equilibrium for copper iodate may be written as,

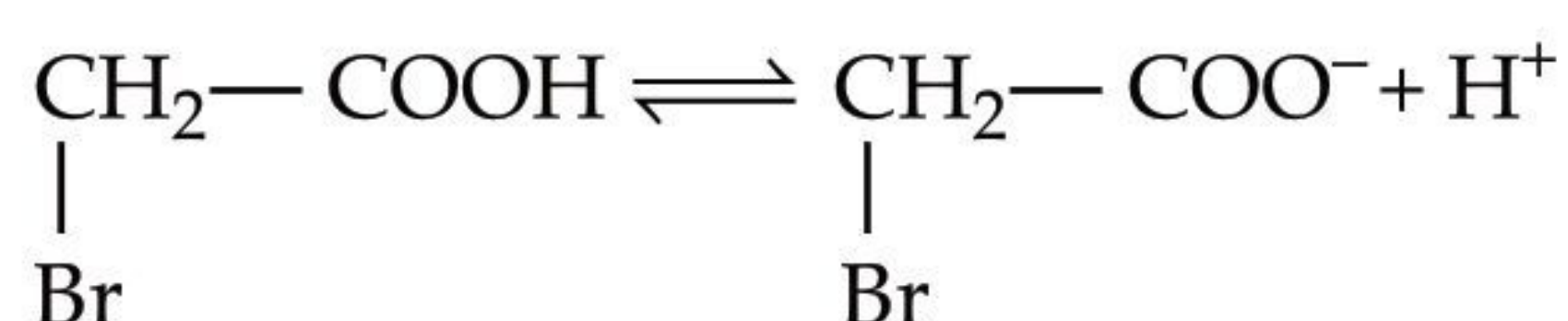


Ionic product of copper iodate

$$= [\text{Cu}^{2+}] [\text{IO}_3^-]^2 = (0.001) (0.001)^2 = 1 \times 10^{-9}$$

Since ionic product ( $1 \times 10^{-9}$ ) is less than  $K_{sp}$  ( $7.4 \times 10^{-8}$ ), therefore, no precipitation will take place.

OR



Initial molar conc :      C                      0                      0  
Eq. molar conc :      C(1 -  $\alpha$ )                      C $\alpha$                       C $\alpha$

C = 0.1 M,  $\alpha = 0.132$ ,  $[\text{H}^+] = C\alpha = 0.0132 \text{ M}$

pH =  $-\log(0.0132) = 1.8794$

$K_a = C\alpha^2$  or  $K_a = 0.1 \times (0.132)^2 = 1.74 \times 10^{-3}$

$\text{p}K_a = -\log K_a = -\log(1.74 \times 10^{-3}) = 2.7595$

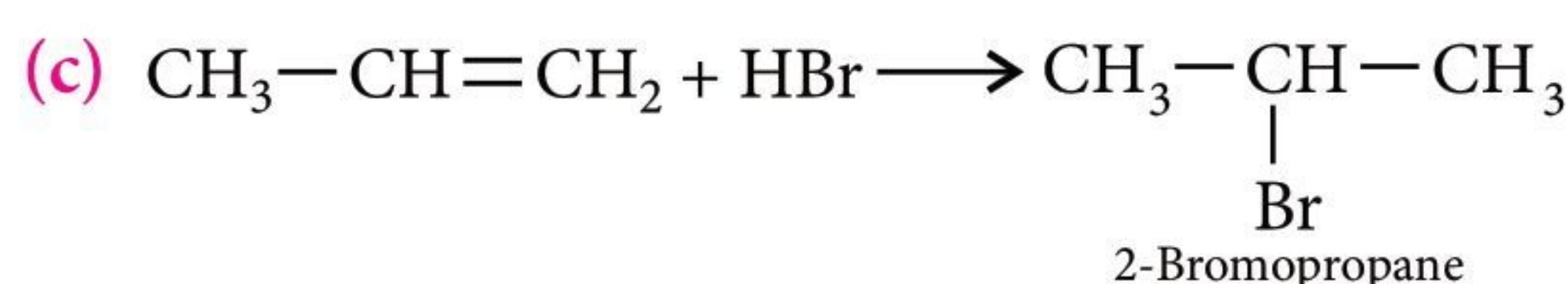
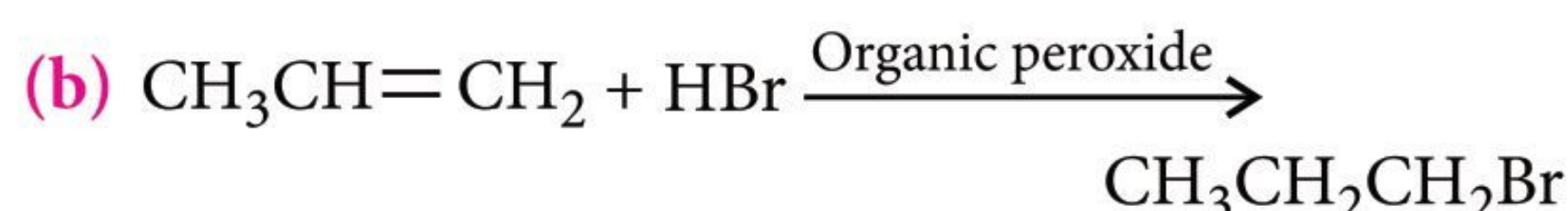
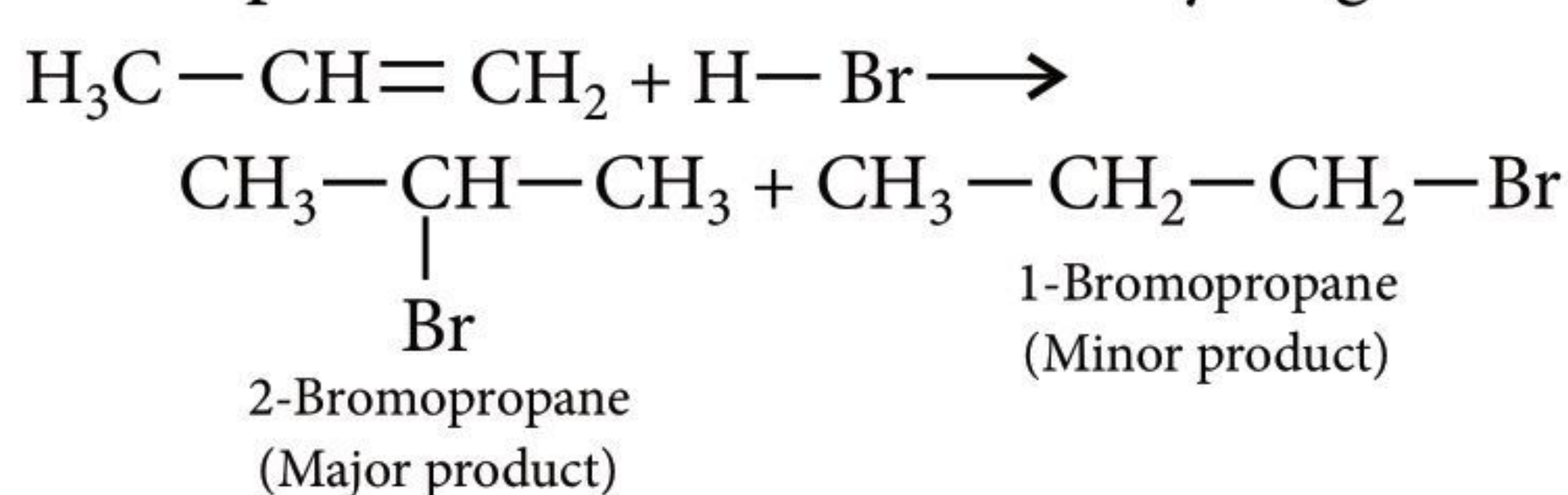
11. (i) The extent to which a real gas deviates from ideal behaviour can be conveniently studied in terms

of 'Z' called the compressibility factor, which is mathematically defined as  $Z = \frac{PV}{nRT}$

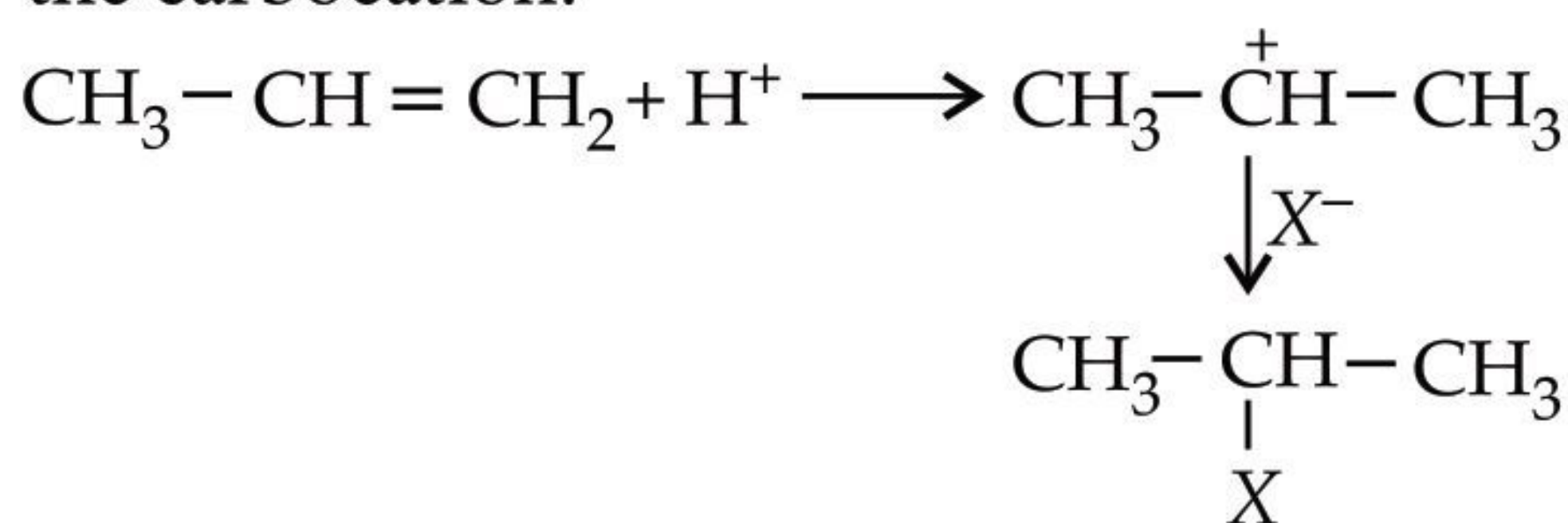
(ii) For an ideal gas, as  $PV = nRT$ , so, the value of  $Z = 1$   
For a non-ideal (real) gas,  $Z \neq 1$ , either  $Z > 1$  or  $Z < 1$

(iii) When  $Z < 1$ , (e.g., for  $\text{CH}_4$ ,  $\text{CO}_2$ , etc.), the gas is said to show negative deviation. This implies that the gas is more compressible than expected from ideal behaviour.

12. (a) Markovnikov's rule states that the positive part of the addendum gets attached to that carbon atom which possesses more number of hydrogen atoms, e.g.,



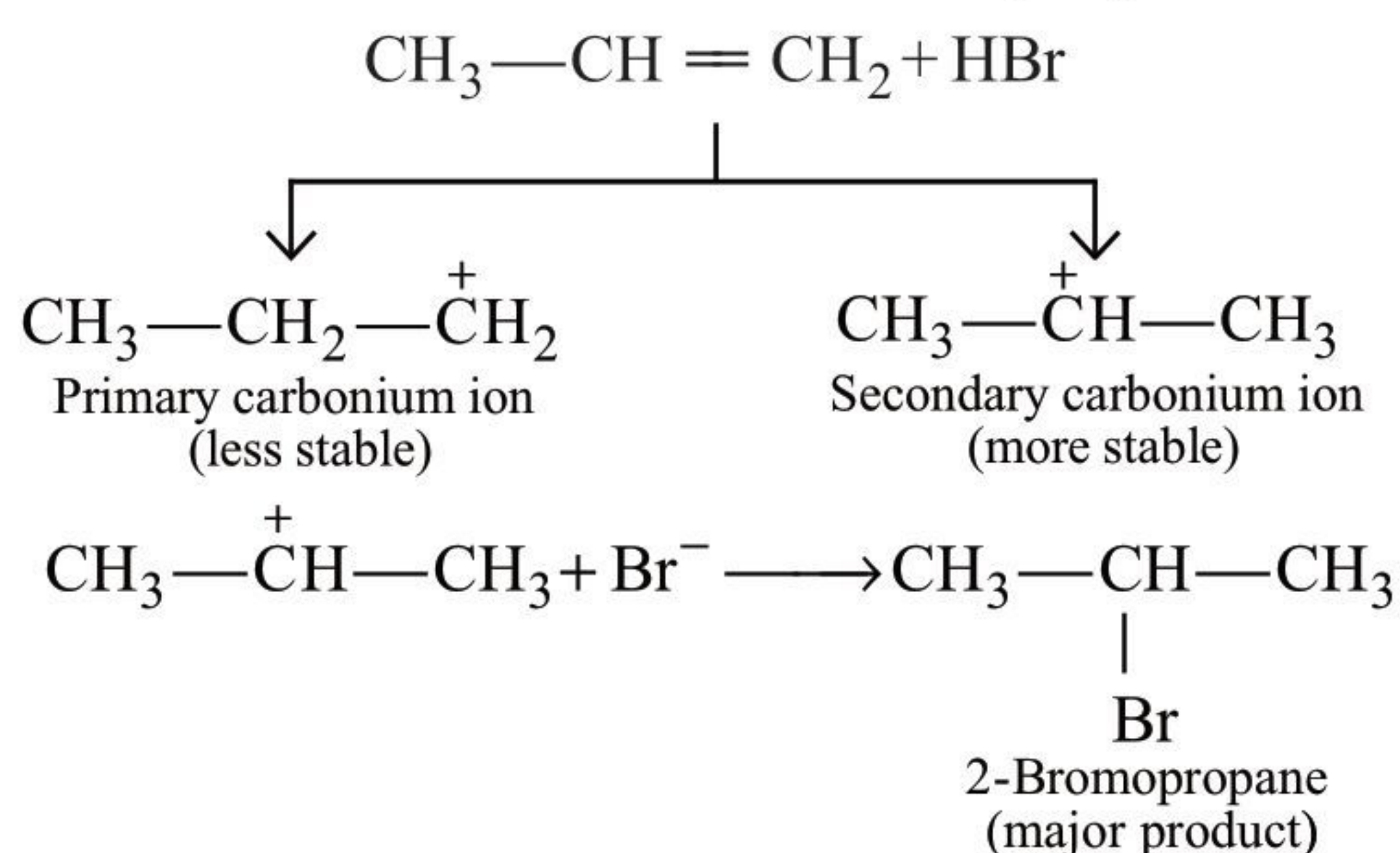
(d) Addition of haloacids to propene leads to the formation of same carbocation due to addition of  $\text{H}^+$  ion first. In the second step,  $\text{X}^-$  ion (nucleophile) attacks the carbocation.



Reactivity of haloacids depends upon the bond dissociation energy of  $\text{H}-\text{X}$  molecule which is least for HI and maximum for HCl, therefore, order of reactivity will be  $\text{HI} > \text{HBr} > \text{HCl}$ .

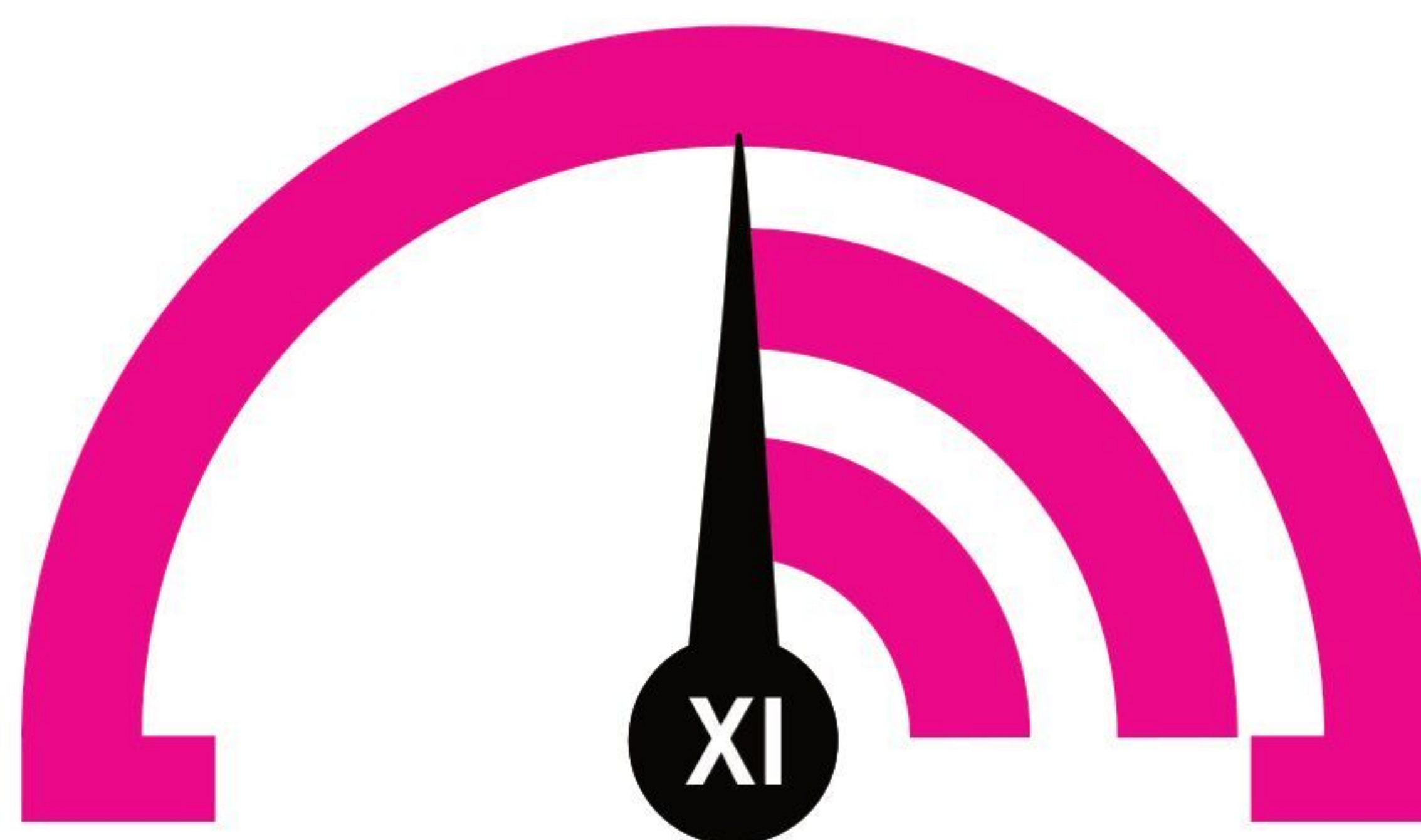
OR

Mechanism of addition of HBr to propene :





# MONTHLY TEST DRIVE



This specially designed column enables students to self analyse their extent of understanding of specified chapters. Give yourself four marks for correct answer and deduct one mark for wrong answer. Self check table given at the end will help you to check your readiness.

Total Marks : 120

## Equilibrium | Redox Reactions

Time Taken : 60 Min.

### NEET

#### Only One Option Correct Type

- Slaked lime,  $\text{Ca}(\text{OH})_2$  is used extensively in sewage treatment. What is the maximum pH that can be established in  $\text{Ca}(\text{OH})_{2(aq)}$ ?  
 $\text{Ca}(\text{OH})_{2(s)} \rightleftharpoons \text{Ca}^{2+}_{(aq)} + 2\text{OH}^{-}_{(aq)}$ ,  $K_{sp} = 5.5 \times 10^{-6}$   
 (a) 1.66 (b) 12.35 (c) 7 (d) 14
- If the volume of the flask in which the given reactions takes place is doubled, in which of the following cases, equilibrium constant is affected?  
 I.  $\text{N}_{2(g)} + 3\text{H}_{2(g)} \rightleftharpoons 2\text{NH}_{3(g)}$   
 II.  $\text{N}_{2(g)} + \text{O}_{2(g)} \rightleftharpoons 2\text{NO}_{(g)}$   
 III.  $\text{PCl}_{5(g)} \rightleftharpoons \text{PCl}_{3(g)} + \text{Cl}_{2(g)}$   
 IV.  $2\text{HI}_{(g)} \rightleftharpoons \text{H}_{2(g)} + \text{I}_{2(g)}$   
 (a) I, II (b) II, III  
 (c) I, III (d) III, IV
- $E^\circ$  values of some redox couples are given below. On the basis of these values choose the correct option.  
 $E^\circ$  values :  $\text{Br}_2 | \text{Br}^- = +1.90 \text{ V}$ ;  $\text{Ag}^+ | \text{Ag}_{(s)} = +0.80 \text{ V}$   
 $\text{Cu}^{2+} | \text{Cu}_{(s)} = +0.34 \text{ V}$ ;  $\text{I}_2(s) | \text{I}^- = +0.54 \text{ V}$   
 (a) Cu will reduce  $\text{Br}^-$  (b) Cu will reduce Ag  
 (c) Cu will reduce  $\text{I}^-$  (d) Cu will reduce  $\text{Br}_2$
- The correct descending order of the heat liberated (in kJ) during the neutralisation of the acids  $\text{CH}_3\text{COOH}$  (W), HF (X),  $\text{HCOOH}$  (Y) and HCN (Z) under identical conditions is  
 (Given  $K_a$  of  $\text{CH}_3\text{COOH} = 1.8 \times 10^{-5}$ ,  $\text{HCOOH} = 1.8 \times 10^{-4}$ ,  $\text{HCN} = 4.9 \times 10^{-10}$  and  $\text{HF} = 3.2 \times 10^{-4}$ )  
 (a)  $Y > X > Z > W$  (b)  $X > Y > W > Z$   
 (c)  $W > X > Y > Z$  (d)  $Z > W > Y > X$
- To prepare a buffer of pH 8.26, the amount of  $(\text{NH}_4)_2\text{SO}_4$  to be added to 500 mL of 0.01 M  $\text{NH}_4\text{OH}$  solution [ $\text{p}K_a(\text{NH}_4^+) = 9.26$ ] is  
 (a) 0.05 mole (b) 0.025 mole  
 (c) 0.10 mole (d) 0.005 mole
- $\text{Cl}_2$  and  $\text{SO}_2$  are pollutants as well as bleaching agents. Their bleaching action is due to  

$\text{SO}_2$	$\text{Cl}_2$
(a) Oxidation	Oxidation
(b) Reduction	Reduction
(c) Oxidation	Reduction
(d) Reduction	Oxidation
- For the equation,  $2A_{(g)} + B_{(g)} \rightleftharpoons 3C_{(g)} + D_{(g)}$  two moles each of A and B were taken into a flask. Which of the following must always be true when the system attains equilibrium?  
 (a)  $[A] = [B]$  (b)  $[A] < [B]$   
 (c)  $[B] = [C]$  (d)  $[A] > [B]$
- A quantity of  $\text{PCl}_5$  was heated in a  $10 \text{ dm}^3$  vessel at  $250^\circ\text{C}$   
 $\text{PCl}_{5(g)} \rightleftharpoons \text{PCl}_{3(g)} + \text{Cl}_{2(g)}$   
 At equilibrium, the vessel contains 0.1 mole of  $\text{PCl}_5$  and 0.2 mole of  $\text{Cl}_2$ . The equilibrium constant of the reaction is  
 (a) 0.05 (b) 0.04  
 (c) 0.02 (d) 0.025
- Which is the best description of the behaviour of bromine in the reaction given below?  
 $\text{H}_2\text{O} + \text{Br}_2 \rightarrow \text{HOBr} + \text{HBr}$   
 (a) Reduced only  
 (b) Proton acceptor only  
 (c) Both oxidised and reduced  
 (d) Oxidised only



10. In the standardization of  $\text{Na}_2\text{S}_2\text{O}_3$  using  $\text{K}_2\text{Cr}_2\text{O}_7$  by iodometry, the equivalent weight of  $\text{K}_2\text{Cr}_2\text{O}_7$  is  
 (a) (molecular weight)/2  
 (b) (molecular weight)/6  
 (c) (molecular weight)/3  
 (d) none of these.
11. At constant temperature, the equilibrium constant ( $K_p$ ) for the decomposition reaction is expressed by  $K_p = 4x^2P/(1 - x^2)$  where  $P$  is pressure,  $x$  is extent of decomposition. Which of the following statements is true?  
 (a)  $K_p$  increases with increase of  $P$ .  
 (b)  $K_p$  increases with increase of  $x$ .  
 (c)  $K_p$  increases with decrease of  $x$ .  
 (d)  $K_p$  remains constant with change in  $P$  or  $x$ .
12. Ionisation constant of  $\text{CH}_3\text{COOH}$  is  $1.7 \times 10^{-5}$  and concentration of  $\text{H}^+$  in certain acetic acid solution is  $3.4 \times 10^{-4}$  M. The concentration of acetic acid solution is  
 (a)  $3.4 \times 10^{-4}$  M (b)  $3.4 \times 10^{-3}$  M  
 (c)  $6.8 \times 10^{-4}$  M (d)  $6.8 \times 10^{-3}$  M

#### Assertion & Reason Type

**Directions :** In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct choice as :

- (a) If both assertion and reason are true and reason is the correct explanation of assertion.  
 (b) If both assertion and reason are true but reason is not the correct explanation of assertion.  
 (c) If assertion is true but reason is false.  
 (d) If both assertion and reason are false.

13. **Assertion :**  $\text{SO}_{2(g)} + \frac{1}{2}\text{O}_{2(g)} \rightleftharpoons \text{SO}_{3(g)} + \text{heat}$

Forward reaction is favoured at high temperature and low pressure.

**Reason :** Reaction is endothermic.

14. **Assertion :** In the reaction between potassium permanganate and potassium iodide, permanganate ions act as oxidising agent.

**Reason :** Oxidation state of manganese changes from +2 to +7 during the reaction.

15. **Assertion :** The decomposition of hydrogen peroxide to form water and oxygen is an example of disproportionation reaction.

**Reason :** The oxygen of peroxide is in -1 oxidation state and it is converted to zero oxidation state in  $\text{O}_2$  and -2 oxidation state in  $\text{H}_2\text{O}$ .

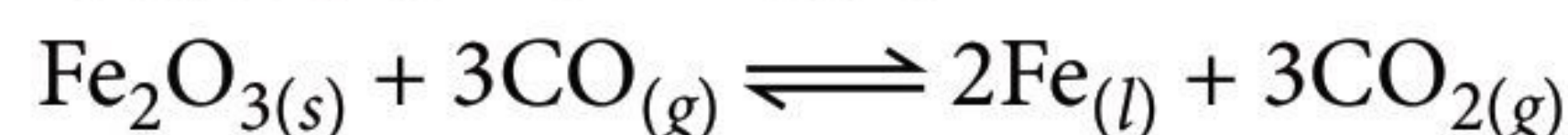
#### JEE MAIN / JEE ADVANCED

##### Only One Option Correct Type

16. Amount of oxalic acid present in a solution can be determined by its titration with  $\text{KMnO}_4$  solution in the presence of  $\text{H}_2\text{SO}_4$ . The titration gives unsatisfactory result when carried out in the presence of  $\text{HCl}$ , because  $\text{HCl}$   
 (a) oxidises oxalic acid to carbon dioxide and water  
 (b) gets oxidised by oxalic acid to chlorine  
 (c) furnishes  $\text{H}^+$  ions in addition to those from oxalic acid  
 (d) reduces permanganate to  $\text{Mn}^{2+}$ .
17. A sample of  $\text{AgCl}$  was treated with 5.00 mL of 1.5 M  $\text{Na}_2\text{CO}_3$  solution to give  $\text{Ag}_2\text{CO}_3$ . The remaining solution contained 0.0026 g of  $\text{Cl}^-$  per litre. Calculate the solubility product of  $\text{AgCl}$ . ( $K_{sp}(\text{Ag}_2\text{CO}_3) = 8.2 \times 10^{-12}$ )  
 (a)  $7.32 \times 10^{-5}$  (b)  $1.71 \times 10^{-10}$   
 (c)  $2.34 \times 10^{-6}$  (d)  $1.34 \times 10^{-10}$
18. In the following disproportionation of  $\text{Cl}_2$  in basic medium  
 $\text{Cl}_2 + 2\text{KOH} \longrightarrow \text{KCl} + \text{KClO} + \text{H}_2\text{O}$   
 equivalent mass of  $\text{Cl}_2$  is  
 (a) 35.50 (b) 71.00 (c) 47.33 (d) 11.83
19. A gas  $X$  at 1 atm is bubbled through a solution containing a mixture of 1 M  $\text{Y}^-$  and 1 M  $\text{Z}^-$  at  $25^\circ\text{C}$ . If the reduction potential of  $\text{Z} > \text{Y} > \text{X}$ , then,  
 (a)  $\text{Y}$  will oxidize  $X$  and not  $Z$   
 (b)  $\text{Y}$  will oxidize  $Z$  and not  $X$   
 (c)  $\text{Y}$  will oxidize both  $X$  and  $Z$   
 (d)  $\text{Y}$  will reduce both  $X$  and  $Z$ .

##### More Than One Options Correct Type

20. The reaction of iron(III) oxide with carbon monoxide occurs in a blast furnace when iron ore is reduced to iron metal :



#### COMIC CAPSULE

**Q:** What did the scientist say when he found 2 isotopes of helium?

**A:** HeHe



Mark out the correct statements.

- (a) Addition of  $\text{Fe}_2\text{O}_3$  does not cause concentration stress.
- (b) Concentration stress due to removal of  $\text{CO}_2$  is relieved on net shifting of equilibrium from right to left.
- (c) Concentration stress due to removal of  $\text{CO}$  is relieved on net shifting of equilibrium from left to right.
- (d) Concentration stress due to removal of  $\text{CO}$  causes first increase then decrease in  $Q_c$ .

21. Which of the following form conjugate acid-base pairs in the right order?

- (a)  $\text{NH}_3, \text{NH}_2^-$  (b)  $\text{S}^{2-}, \text{HS}^-$
- (c)  $\text{HCO}_3^-, \text{CO}_3^{2-}$  (d)  $\text{HNO}_3, \text{NO}_3^-$

22. An oxidising agent in a chemical reaction undergoes

- (a) gain of electrons
- (b) loss of electron
- (c) a decrease in oxidation number
- (d) an increase in oxidation number.

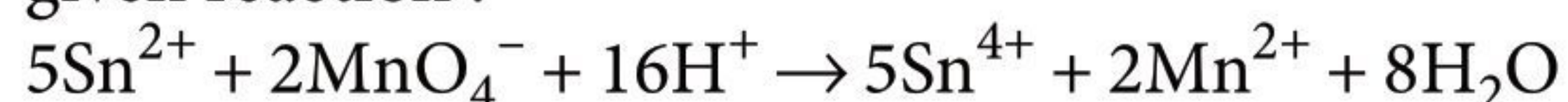
23. When  $\text{Cl}_2$  is passed through hot  $\text{NaOH}$ , oxidation number of  $\text{Cl}$  changes from

- (a) -1 to 0 (b) 0 to -1
- (c) 0 to +5 (d) 0 to +7

#### Integer / Numerical Value Type

24. A buffer solution with  $\text{pH} = 9$  is to be prepared by mixing  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{OH}$ . Calculate the number of moles of  $\text{NH}_4\text{Cl}$  that should be added to one litre of 1.0 M  $\text{NH}_4\text{OH}$  ( $K_b = 1.8 \times 10^{-5}$ ).

25. Calculate the volume of 0.150 M  $\text{KMnO}_4$  solution in millilitres required to react completely with 17.5 mL of 0.150 M  $\text{SnCl}_2$  solution according to the given reaction :



26. Calculate the pH of a 0.10 M solution of  $\text{Na}_2\text{SO}_4$ .  $K_a(\text{H}_2\text{SO}_4) = 1 \times 10^{-2}$ . Assume hydrolysis of  $\text{SO}_4^{2-}$  to  $\text{HSO}_4^-$ .

#### Comprehension Type

In case of strong acid or strong base we can calculate pH by the formula  $\text{pH} = -\log_{10}[\text{H}^+]$ .

When a salt is dissolved in a solvent, it first dissociates into its ions and if these ions chemically react with water then this process is called hydrolysis.

Hydrolysis of salt of weak acid + strong base,

$$\text{pH} = 7 + \frac{1}{2} \text{p}K_a + \frac{1}{2} \log C$$

Hydrolysis of salt of weak base + strong acid,

$$\text{pH} = 7 - \frac{1}{2} \text{p}K_b - \frac{1}{2} \log C$$

Hydrolysis of salt of weak acid + weak base,

$$\text{pH} = 7 + \frac{1}{2} \text{p}K_a - \frac{1}{2} \text{p}K_b$$

In case of buffer solution

**Acidic buffer :**  $\text{pH} = \text{p}K_a + \log \frac{[\text{salt}]}{[\text{acid}]}$

**Basic buffer :**  $\text{pOH} = \text{p}K_b + \log \frac{[\text{salt}]}{[\text{base}]}$

**Data :** -  $K_a(\text{CH}_3\text{COOH}) = 1.8 \times 10^{-5}$ ;  $K_b(\text{NH}_4\text{OH}) = 1.8 \times 10^{-5}$ ;  $\text{p}K_a = 4.7$ ,  $\text{p}K_b = 4.7$ ,  $\log 2 = 0.3010$ ;  $\log 4 = 0.6020$ ;  $\log 5 = 0.6990$

27. When 50 mL of 0.05 M  $\text{NaOH}$  is added in 50 mL, of 0.10 M  $\text{CH}_3\text{COOH}$  solution, pH becomes

- (a) 12.3 (b) 4.7
- (c) 8.7 (d) 1.6

28. When 50 mL of 0.10 M  $\text{NH}_4\text{OH}$  is added in 50 mL of 0.05 M  $\text{HCl}$  solution, pH becomes

- (a) 1.6021 (b) 12.39
- (c) 4.7 (d) 9.3

#### Form IV

- |   |  |
|---|--|
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For MTG Learning Media Pvt. Ltd.  
Mahabir Singh  
Director



### Matrix Match Type

29. Match column-I with column-II and choose the correct option.

Column-I	Column-II
A. $\text{N}_{2(g)} + 3\text{H}_{2(g)} \rightleftharpoons 2\text{NH}_{3(g)}; \Delta H = -\text{ve}$	p. $K$ increases with increase in temperature.
B. $\text{N}_{2(g)} + \text{O}_{2(g)} \rightleftharpoons 2\text{NO}_{(g)}; \Delta H = +\text{ve}$	q. $K$ decreases with increase in temperature.
C. $\text{A}_{(g)} + \text{B}_{(g)} \rightleftharpoons 2\text{C}_{(g)} + \text{D}_{(g)}; \Delta H = -\text{ve}$	r. Pressure has no effect.
D. $\text{PCl}_{5(g)} \rightleftharpoons \text{PCl}_{3(g)} + \text{Cl}_{2(g)}; \Delta H = +\text{ve}$	s. Moles of product increase due to addition of inert gas at constant pressure.

- (a)  $\text{A} \rightarrow \text{p, s}; \text{B} \rightarrow \text{q}; \text{C} \rightarrow \text{r}; \text{D} \rightarrow \text{q, s}$   
 (b)  $\text{A} \rightarrow \text{q}; \text{B} \rightarrow \text{p, r}; \text{C} \rightarrow \text{q, s}; \text{D} \rightarrow \text{p, s}$   
 (c)  $\text{A} \rightarrow \text{p}; \text{B} \rightarrow \text{q, r}; \text{C} \rightarrow \text{q, s}; \text{D} \rightarrow \text{s}$   
 (d)  $\text{A} \rightarrow \text{q, r}; \text{B} \rightarrow \text{p}; \text{C} \rightarrow \text{q, s}; \text{D} \rightarrow \text{p, r}$

30. Match column I with column II for oxidation states of the central atoms and choose the correct option.

Column I	Column II
(i) $\text{Cr}_2\text{O}_7^{2-}$	(a) +3
(ii) $\text{MnO}_4^-$	(b) +4
(iii) $\text{VO}_3^-$	(c) +5
(iv) $\text{FeF}_6^{3-}$	(d) +6
	(e) +7
(a) (i) $\rightarrow$ (d); (ii) $\rightarrow$ (c); (iii) $\rightarrow$ (a); (iv) $\rightarrow$ (b)	
(b) (i) $\rightarrow$ (d); (ii) $\rightarrow$ (e); (iii) $\rightarrow$ (c); (iv) $\rightarrow$ (a)	
(c) (i) $\rightarrow$ (e); (ii) $\rightarrow$ (a); (iii) $\rightarrow$ (c); (iv) $\rightarrow$ (d)	
(d) (i) $\rightarrow$ (e); (ii) $\rightarrow$ (b); (iii) $\rightarrow$ (d); (iv) $\rightarrow$ (c)	

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No. of questions attempted .....  
 No. of questions correct .....  
 Marks scored in percentage .....

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90-75%	GOOD WORK !	You can score good in the final exam.
74-60%	SATISFACTORY !	You need to score more next time.
< 60%	NOT SATISFACTORY!	Revise thoroughly and strengthen your concepts.

## Scientist of the Month

### Peter Joseph William Debye

#### Early Life and Education

- Peter Joseph William Debye was born in Maastricht, Netherlands on March 24, 1884. Debye enrolled in the Aachen University of Technology in 1901. In 1905, he completed his first degree in electrical engineering. He published his first paper, a mathematically elegant solution of a problem involving eddy currents, in 1907. At Aachen, he studied under the theoretical physicist Arnold Sommerfeld, who later claimed that his most important discovery was Peter Debye.
- In 1906, Sommerfeld received an appointment at Munich, Bavaria, and took Debye with him as his assistant. Debye got his Ph.D. with a dissertation on radiation pressure in 1908. In 1910, he derived the Planck radiation formula using a method which Max Planck agreed was simpler than his own.



Peter Joseph William Debye  
(24 March 1884 - 2 November 1966)

#### Scientific Contributions

- His first major scientific contribution was the application of the concept of dipole moment to the charge distribution in asymmetric molecules in 1912, developing equations relating dipole moments to temperature

and dielectric constant. In consequence, the units of molecular dipole moments are termed debyes in his honor.

- In 1912, he extended Albert Einstein's theory of specific heat to lower temperatures by including contributions from low-frequency phonons.
- In 1913, he extended Niels Bohr's theory of atomic structure, introducing elliptical orbits, a concept also introduced by Arnold Sommerfeld.
- In 1914-1915, Debye calculated the effect of temperature on X-ray diffraction patterns of crystalline solids with Paul Scherrer.
- In 1923, Debye developed a theory to explain the Compton effect, the shifting of the frequency of X-rays when they interact with electrons.
- Much of Debye's work at Cornell concerned the use of light-scattering techniques (derived from his X-ray scattering work of years earlier) to determine the size and molecular weight of polymer molecules. This started as a result of his research during World War II on synthetic rubber, but was extended to proteins and other macromolecules.

#### Awards and Honors

- 1930 – Rumford Medal for work relating to specific heats and X-ray spectroscopy
- 1937 – Franklin Medal from The Franklin Institute.
- 1936 – Nobel Prize in Chemistry (entry at nobelprize.org) "for his contributions to the study of molecular structure," primarily referring to his work on dipole moments and X-ray diffraction
- 1963 – Priestley Medal
- 1965 – National Medal of Science
- 1982 – Alpha Chi Sigma Hall of Fame



# GET SET GO NEET

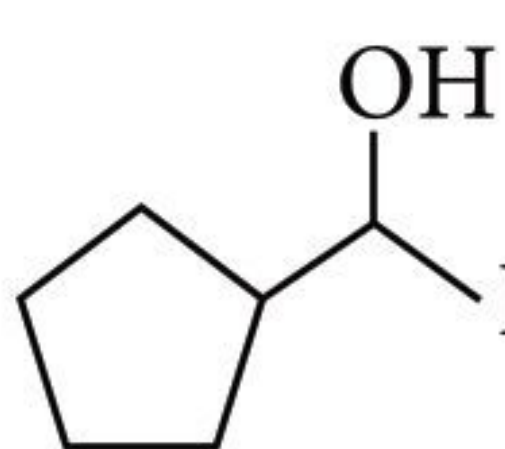


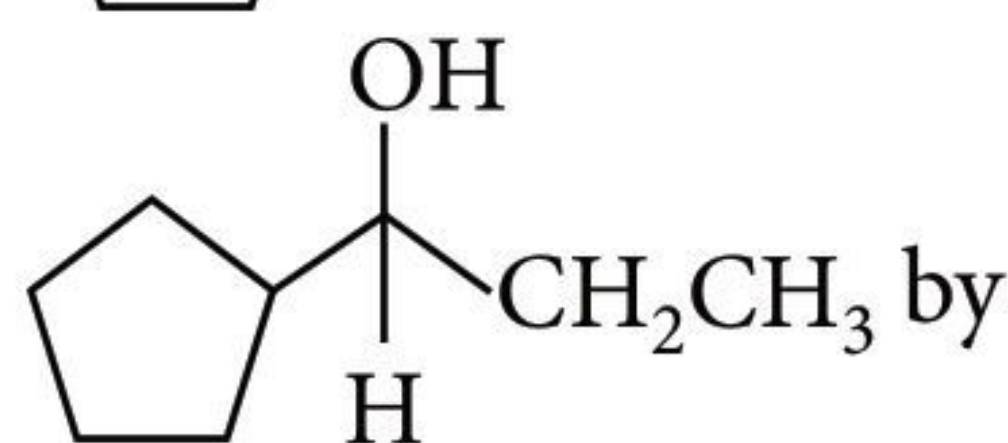
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1. The equivalent conductance of NaCl, HCl and  $\text{C}_2\text{H}_5\text{COONa}$  at infinite dilution are 126.45, 426.16 and  $91 \text{ ohm}^{-1} \text{ cm}^2$  respectively. The equivalent conductance of  $\text{C}_2\text{H}_5\text{COOH}$  is

- (a)  $201.28 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$
- (b)  $390.71 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$
- (c)  $698.28 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$
- (d)  $540.48 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$

2.  can be effectively converted to



- (a)  $\text{CrO}_3$  at  $300^\circ\text{C}$ ,  $\text{CH}_3\text{CH}_2\text{OH}$ ,  $\text{H}_2\text{SO}_4/180^\circ\text{C}$
- (b) hot, conc.  $\text{KMnO}_4$  followed by  $\text{C}_2\text{H}_5\text{MgBr}$ ,  $\text{H}_3\text{O}^+$
- (c)  $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}^+$ ,  $\text{CH}_3\text{CH}_2\text{Br}$ ,  $\text{C}_2\text{H}_5\text{O}^-$
- (d)  $\text{Cu}$  at  $300^\circ\text{C}$ ,  $\text{CH}_3\text{CH}_2\text{MgBr}$ ,  $\text{H}_3\text{O}^+$ .

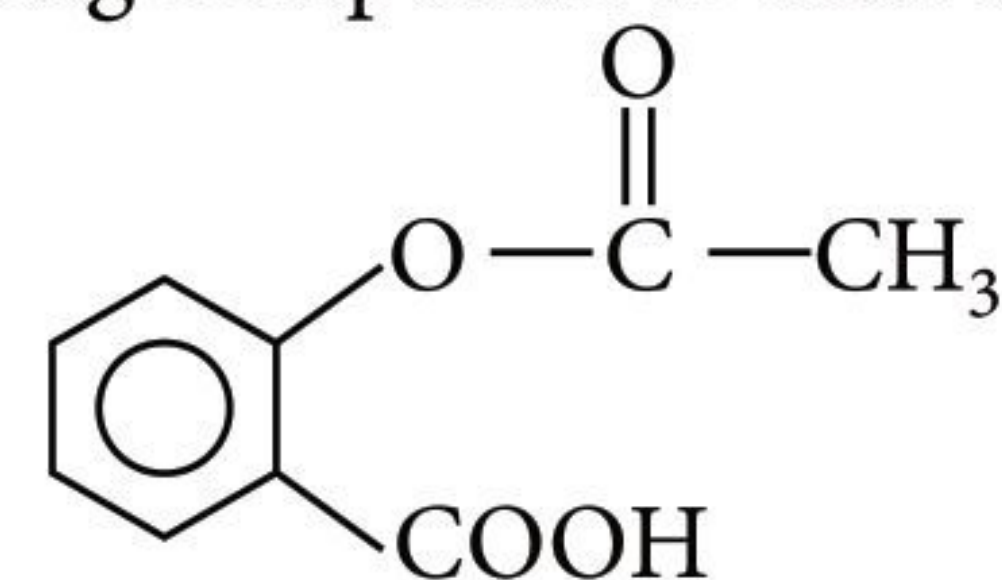
3. Consider the following statements.

- (i)  $\text{Lu}(\text{OH})_3$  is the least basic among hydroxides of lanthanides.
- (ii)  $\text{Eu}^{2+}$  is a good reducing agent in solution.
- (iii) Lanthanides have high densities.
- (iv)  $\text{Ce}^{4+}$  can act as a reducing agent in solution.

Which of the given statements is/are true?

- (a) Only (i) and (iv)
- (b) Only (i), (ii) and (iii)
- (c) Only (iii) and (iv)
- (d) Only (iv)

4. The following compound is used as



- (a) an anti-inflammatory compound
- (b) analgesic
- (c) hypnotic
- (d) antiseptic.

5. Which of the following is not correct ?

- (a)  $[\text{Fe}(\text{CN})_6]^{3-}$  is weakly paramagnetic.
- (b)  $[\text{Fe}(\text{CN})_6]^{4-}$  is strongly paramagnetic.
- (c)  $[\text{Ni}(\text{CN})_4]^{2-}$  is diamagnetic.
- (d)  $[\text{NiCl}_4]^{2-}$  is paramagnetic.

6. Match list I with list II and select the correct answer.

## List I

- (A) Cyanide process
- (B) Floatation process
- (C) Electrolytic reduction
- (D) Zone refining

## List II

- (i) Ultrapure Ge
- (ii) Extraction of Al
- (iii) Pine oil
- (iv) Extraction of Au

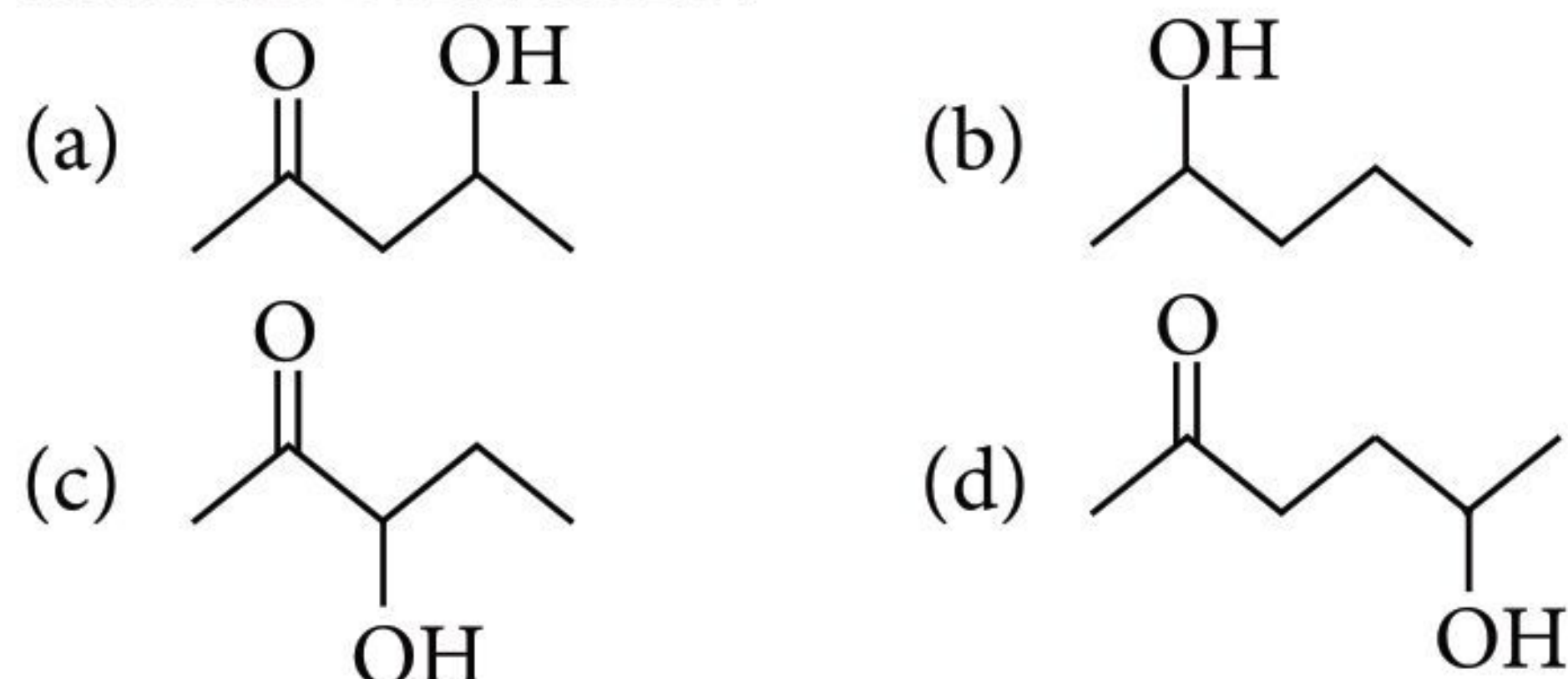


- (a) (A)-(iii), (B)-(iv), (C)-(i), (D)-(ii)  
 (b) (A)-(iv), (B)-(iii), (C)-(ii), (D)-(i)  
 (c) (A)-(iii), (B)-(ii), (C)-(iv), (D)-(i)  
 (d) (A)-(ii), (B)-(i), (C)-(iii), (D)-(iv)

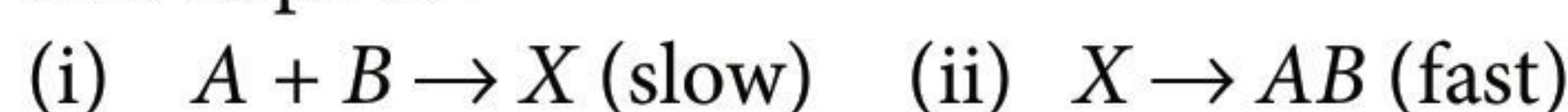
7. Determine the osmotic pressure of a solution prepared by dissolving 25 mg of  $K_2SO_4$  in 2 litres of water at  $25^\circ C$ , assuming that it is completely dissociated.

- (a)  $5.27 \times 10^{-3}$  atm (b)  $1.55 \times 10^{-3}$  atm  
 (c)  $2.67 \times 10^{-3}$  atm (d)  $1.54 \times 10^{-4}$  atm

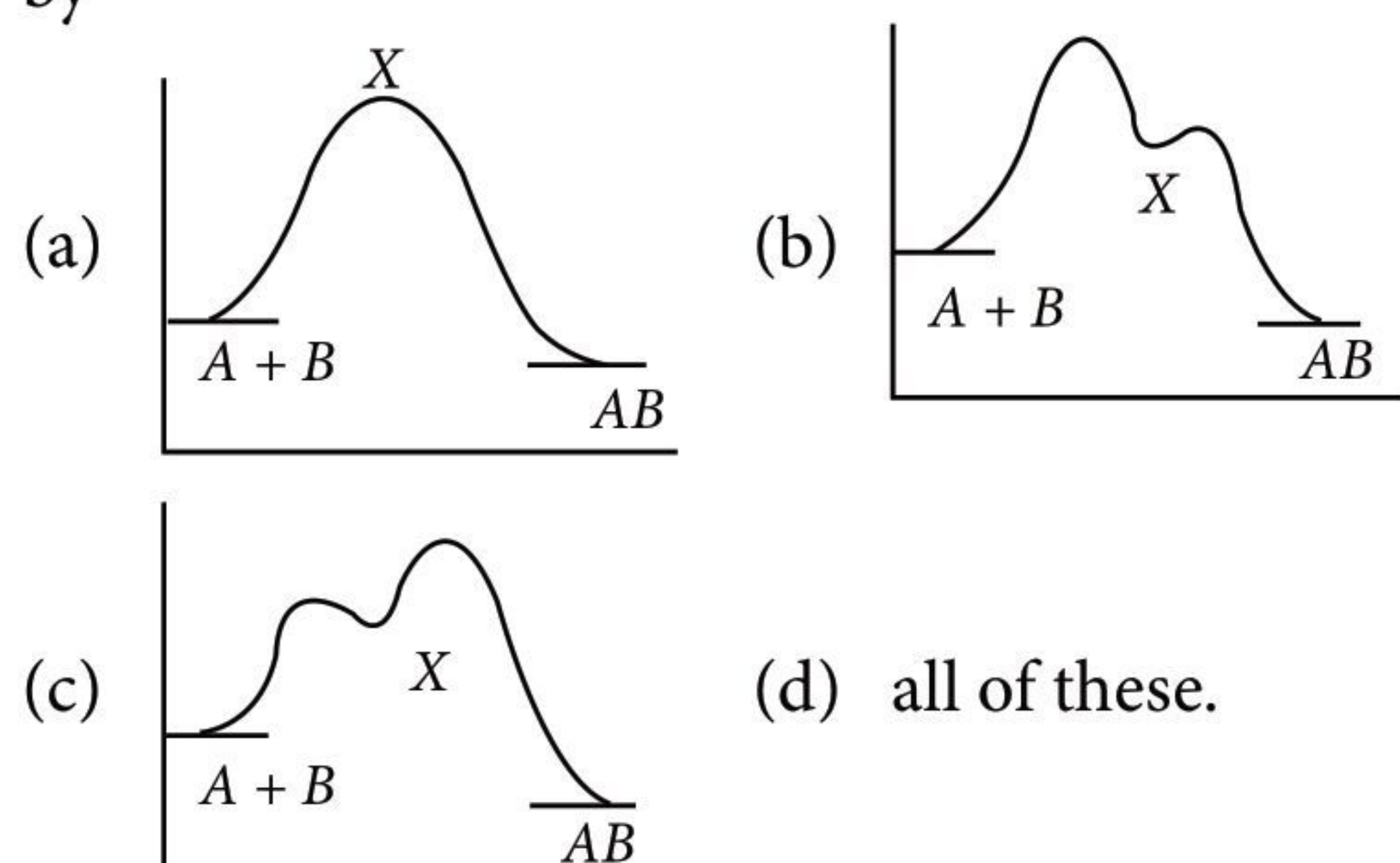
8. Which of the following is most readily dehydrated in acidic conditions?



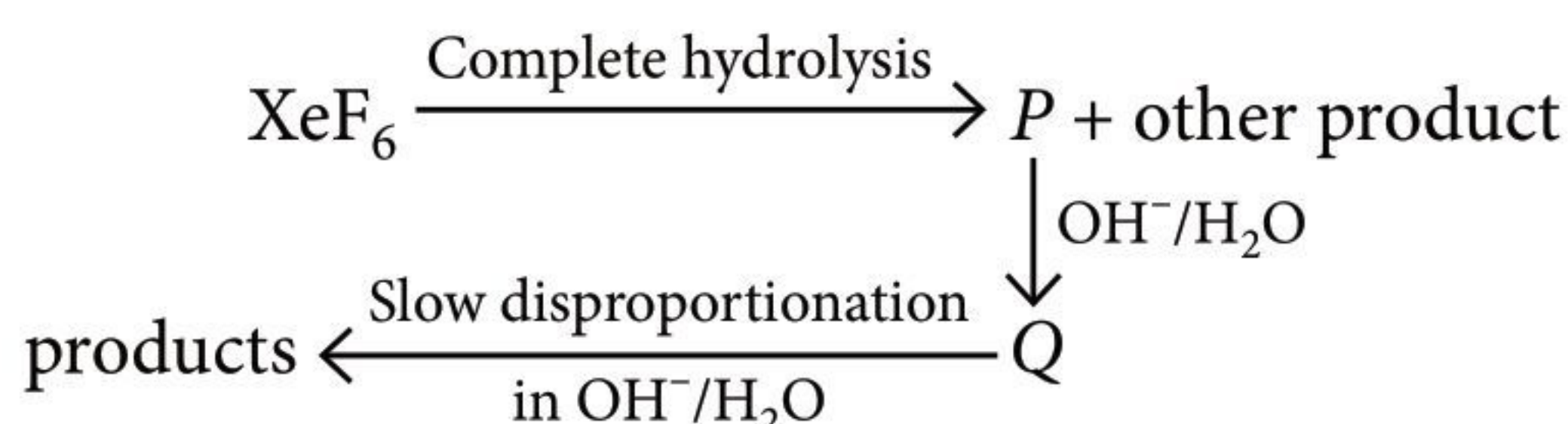
9. For an exothermic chemical reaction occurring in two steps as :



The progress of the reaction can be best described by



10. Under ambient conditions, the total number of gases released as products in the final step of the reaction scheme shown below is



- (a) 0 (b) 1 (c) 2 (d) 3

11. A metal crystallises in a face centred cubic unit cell with  $a = 0.560$  nm. The density of the metal if it contains 0.1% Schottky defect is

(Atomic mass of metal = 40 g/mol)

- (a)  $1.34 \text{ g/cm}^3$  (b)  $1.51 \text{ g/cm}^3$   
 (c)  $2.59 \text{ g/cm}^3$  (d)  $2.68 \text{ g/cm}^3$

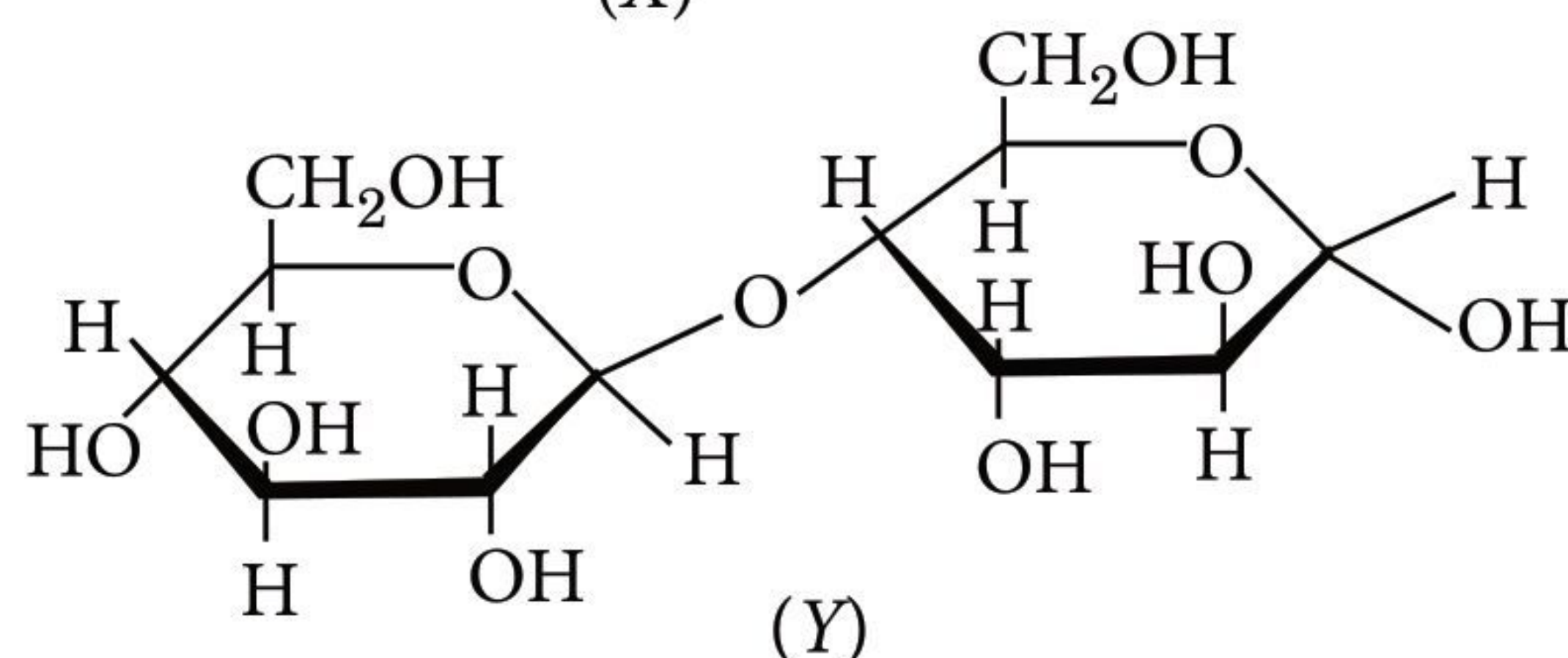
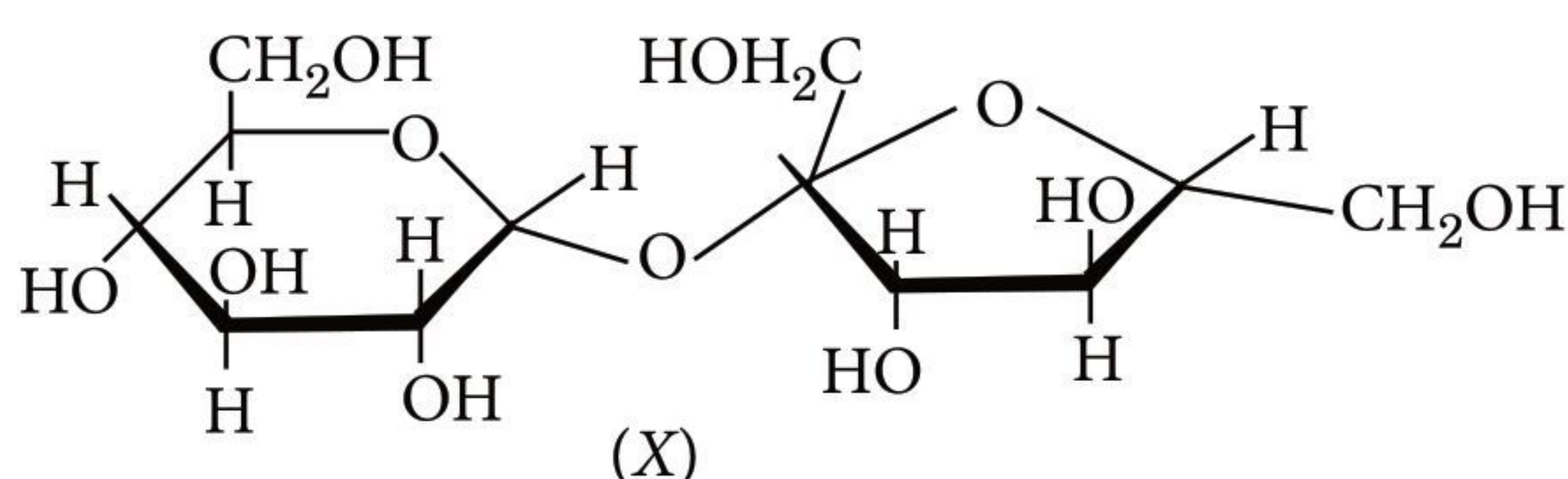
12. Amines are well known to be stronger bases and nucleophiles than alkenes. Why do enamines, such as 1-dimethylaminocyclopentene, preferentially react with electrophiles at a double bond carbon rather than at nitrogen?

- (a) The nitrogen is sterically hindered by alkyl substituents.  
 (b) Nitrogen is more electronegative than carbon.  
 (c) The carbocation formed by electrophilic attack at C-2 is stabilized by  $\pi$ -bonding with the lone pair of electrons on nitrogen.  
 (d) Ammonium cations are less stable than carbocations.

13. On adding  $AgNO_3$  solution to KI solution, a negatively charged colloidal sol will be formed in which of the following conditions?

- (a) 100 mL of 0.1 M  $AgNO_3$  + 100 mL of 0.1 M KI  
 (b) 100 mL of 0.1 M  $AgNO_3$  + 50 mL of 0.2 M KI  
 (c) 100 mL of 0.2 M  $AgNO_3$  + 100 mL of 0.1 M KI  
 (d) 100 mL of 0.1 M  $AgNO_3$  + 100 mL of 0.15 M KI

14. The correct statements about the following sugars X and Y is/are

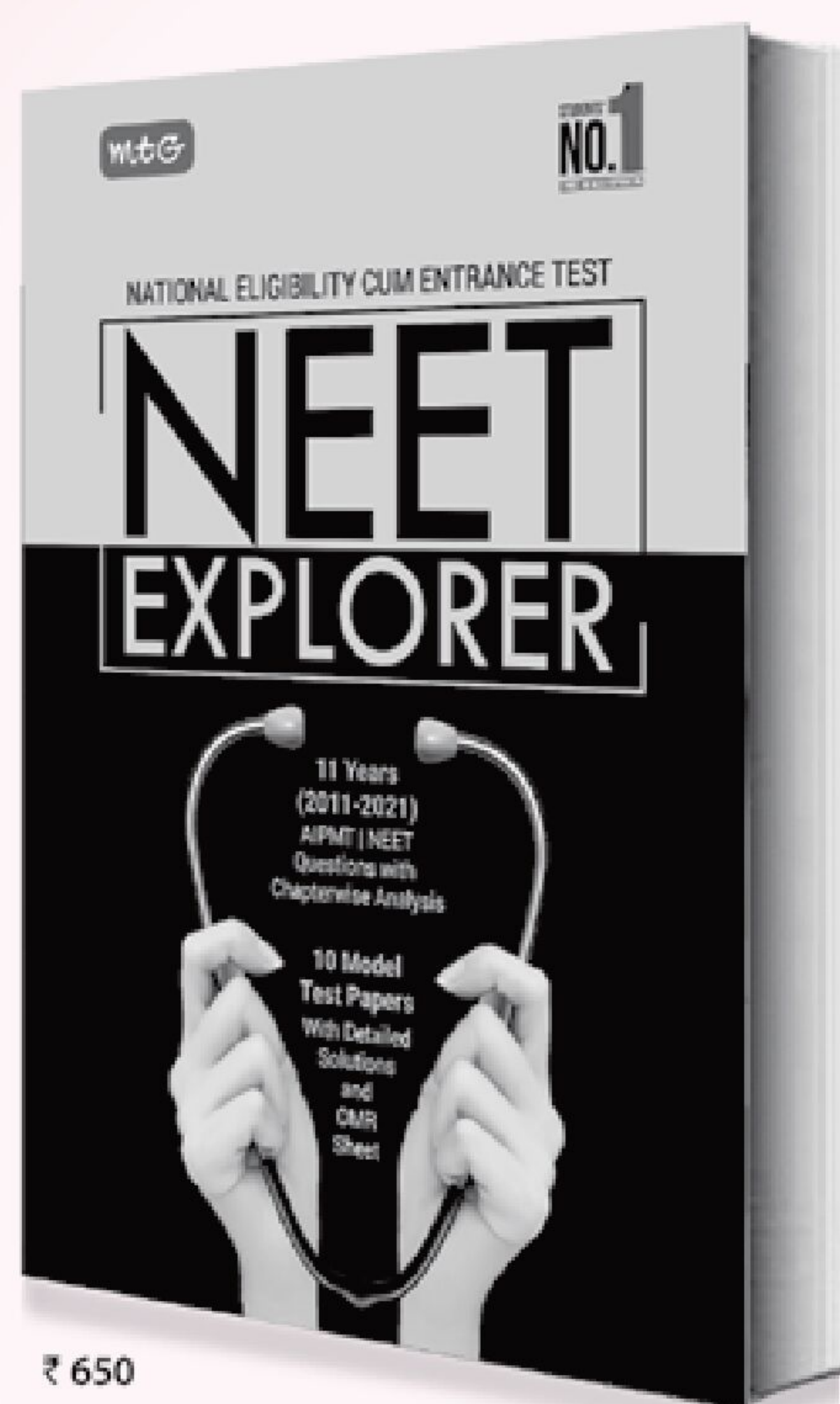


- I. (X) is a reducing sugar and (Y) is a non-reducing sugar  
 II. (X) is a non-reducing sugar and (Y) is a reducing sugar  
 III. The glycosidic linkages in (X) and (Y) are  $\alpha$  and  $\beta$ -respectively  
 IV. The glycosidic linkages in (X) and (Y) are  $\beta$  and  $\alpha$ -respectively  
 (a) Only I (b) Only III & IV  
 (c) Only III (d) Only II & III

15. The structure of the major product formed in the following reaction is



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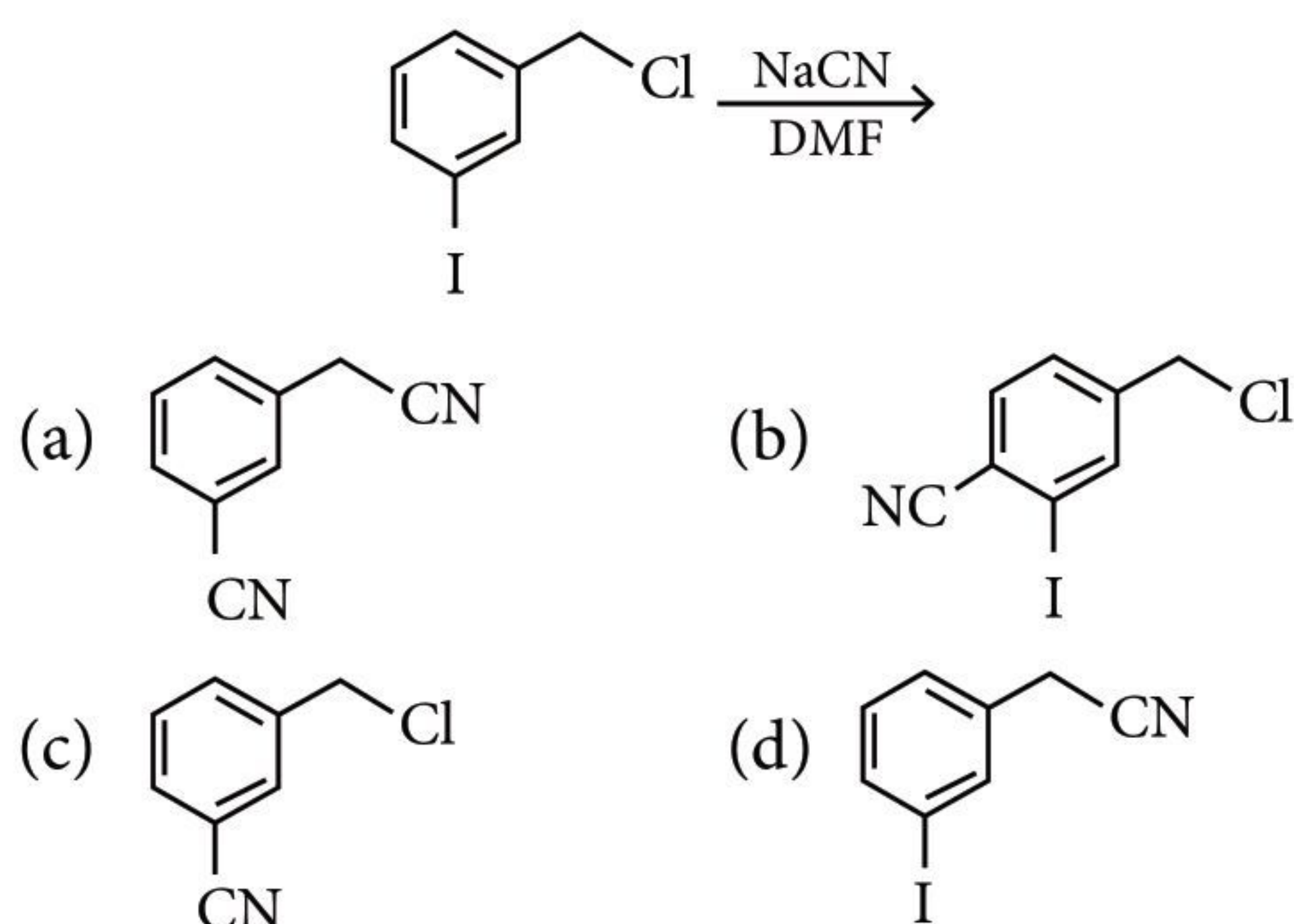


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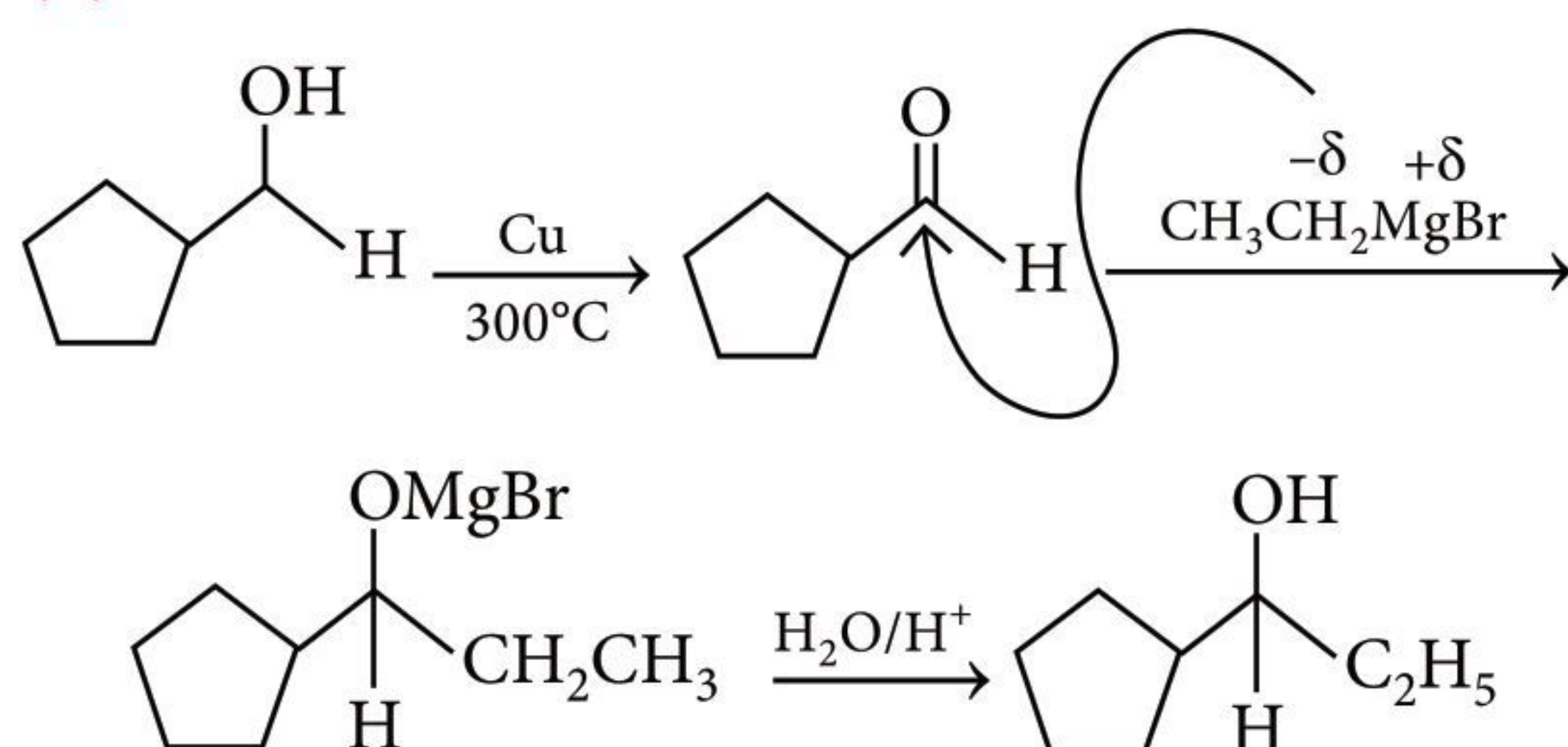




### SOLUTIONS

1. (b) :  $\Lambda_{\text{C}_2\text{H}_5\text{COOH}}^\circ = \Lambda_{\text{C}_2\text{H}_5\text{COONa}}^\circ + \Lambda_{\text{HCl}}^\circ - \Lambda_{\text{NaCl}}^\circ$   
 $= 91 + 426.16 - 126.45$   
 $= 390.71 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$

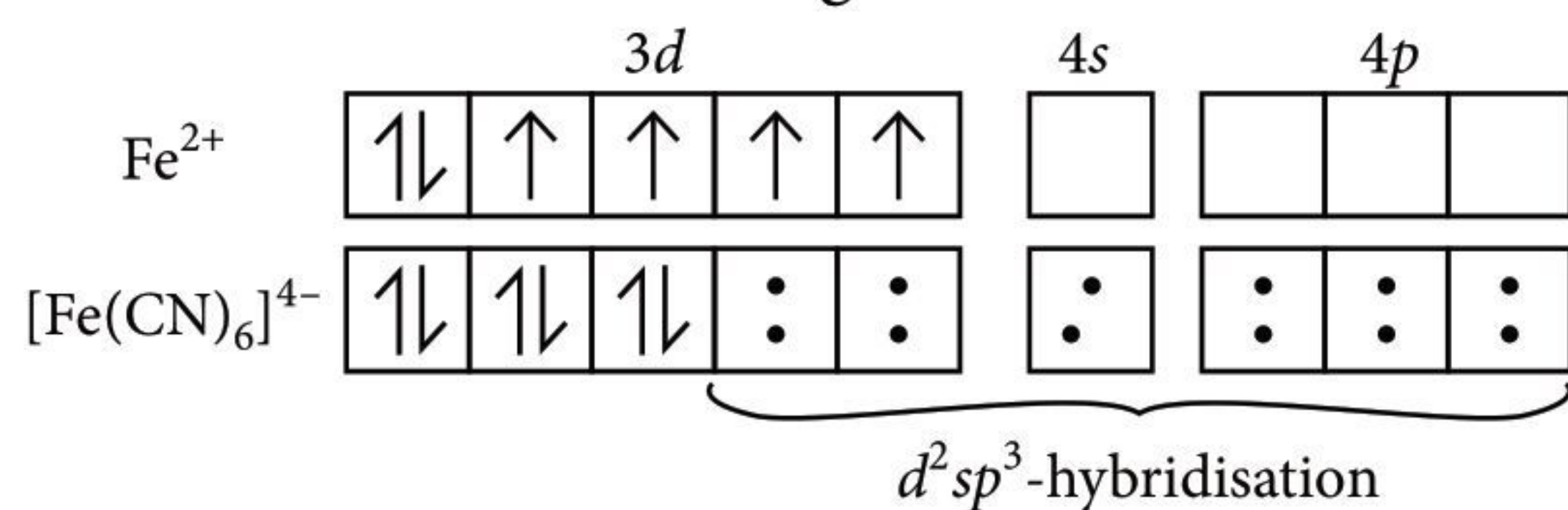
2. (d) :



3. (b) :  $\text{Ce}^{4+}$  acts as a good oxidising agent.

4. (b)

5. (b) :  $[\text{Fe}(\text{CN})_6]^{4-}$  involves  $d^2sp^3$  hybridization. As  $\text{CN}^-$  is a strong field ligand, the pairing of electrons occurs, thus, it is a diamagnetic ion.



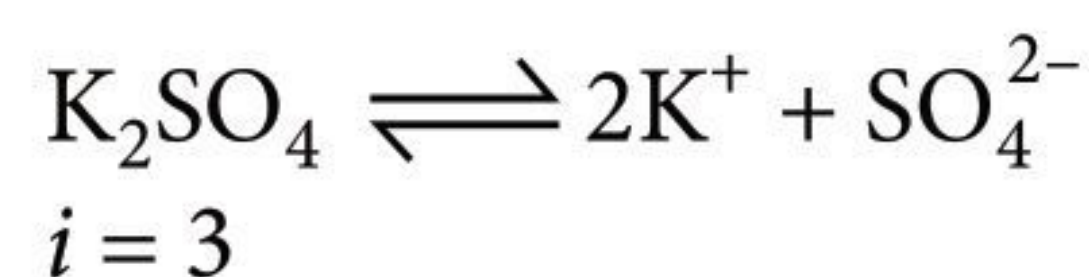
In  $[\text{Fe}(\text{CN})_6]^{3-}$ ,  $3d$ -orbitals have one unpaired electron thus, it is weakly paramagnetic.

In  $[\text{Ni}(\text{CN})_4]^{2-}$ ,  $3d$ -orbitals do not have unpaired electron resulting it is a diamagnetic ion.

In  $[\text{NiCl}_4]^{2-}$ ,  $3d$ -orbitals have two unpaired electrons due to influence of weak ligand ( $\text{Cl}^-$ ) resulting in a paramagnetic ion.

6. (b) : Cyanide process – Extraction of Au  
 Floatation process – Pine oil  
 Electrolytic reduction – Extraction of Al  
 Zone refining – Ultrapure Ge

7. (a) : If  $\text{K}_2\text{SO}_4$  is completely dissociated,



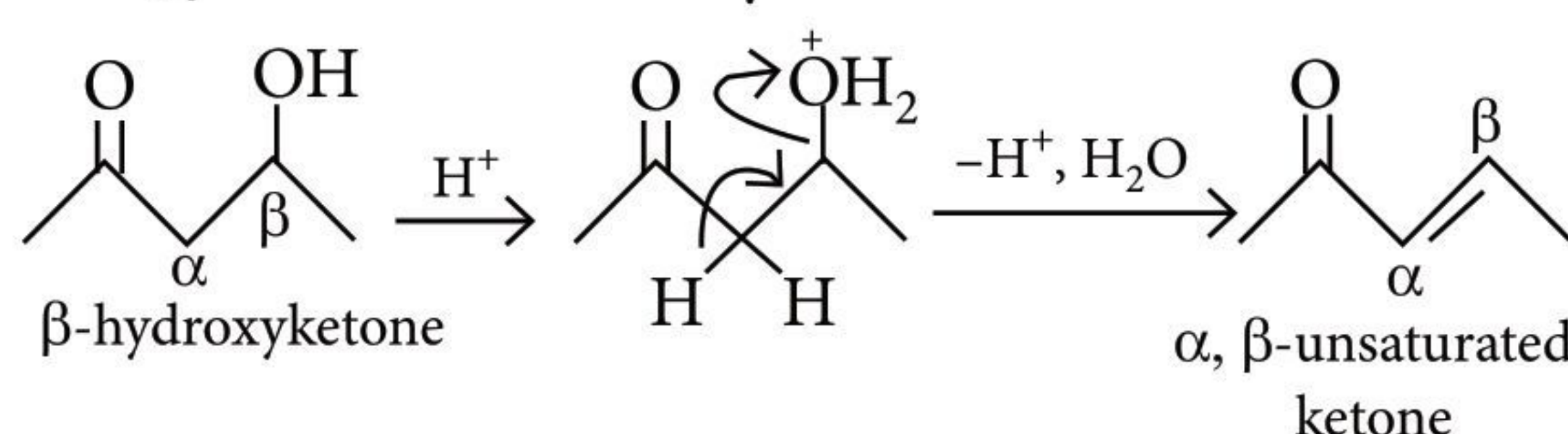
$$\text{Mol. mass of } \text{K}_2\text{SO}_4 = 2 \times 39 + 32 + 4 \times 16 = 174 \text{ g mol}^{-1}$$

$$\pi = i CRT$$

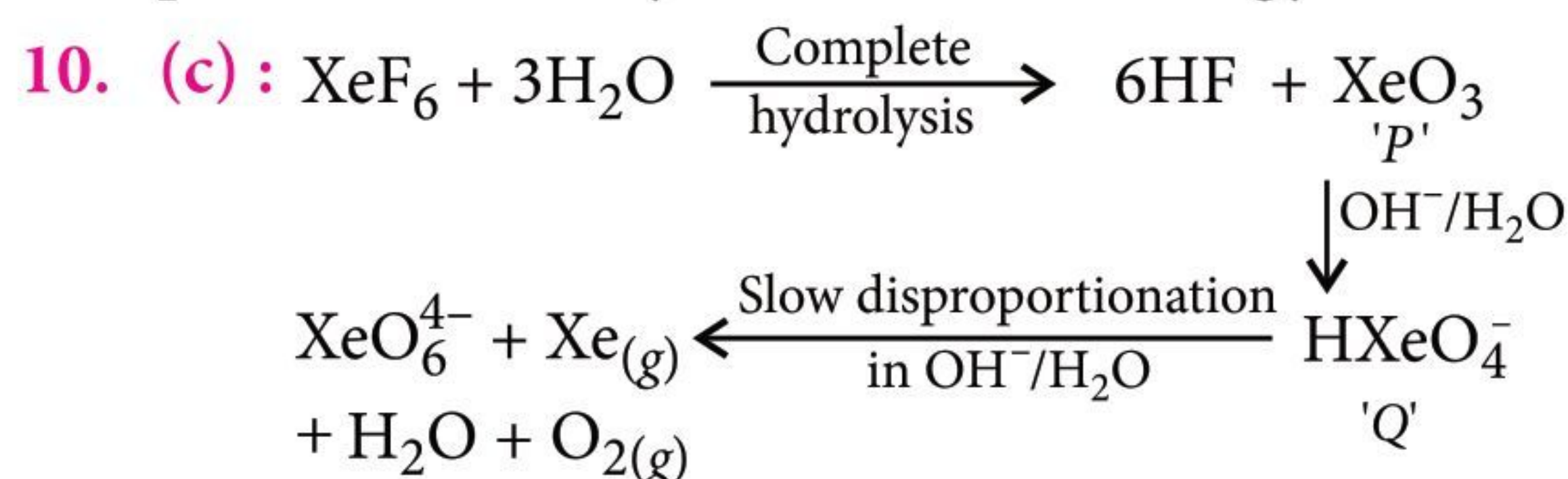
$$= i \frac{W_B \times RT}{M_B \times V} = \frac{3 \times 25 \times 10^{-3} \times 0.082 \times 298}{174 \times 2.0}$$

$$= 5.27 \times 10^{-3} \text{ atm}$$

8. (a) : Aldols, i.e.,  $\beta$ -hydroxyaldehydes or  $\beta$ -hydroxyketones readily undergo dehydration to form  $\alpha, \beta$ -unsaturated aldehydes or ketones.



9. (b) : As conversion of X to AB is fast, it means the process has a very low activation energy.



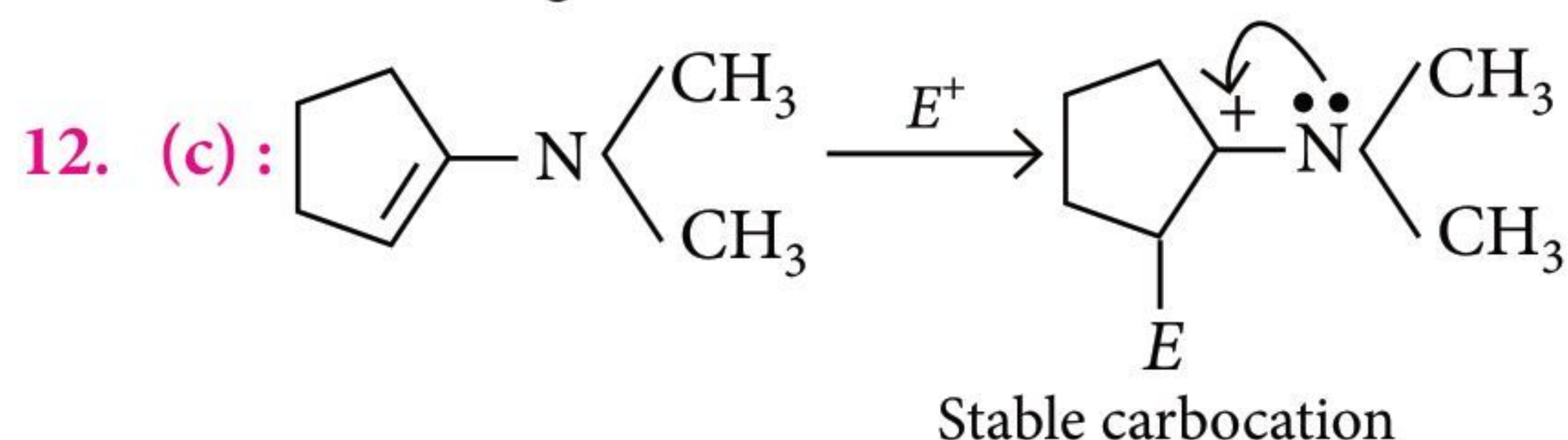
11. (b) : Due to Schottky defect, the vacant spaces will increase, resulting decrease in number of atoms per unit cell.

$$\text{In this case, } Z = \left( 4 - \frac{4 \times 0.1}{100} \right) = 3.996$$

$$\text{Density, } \rho = \frac{Z \times M}{N_0 \times a^3}$$

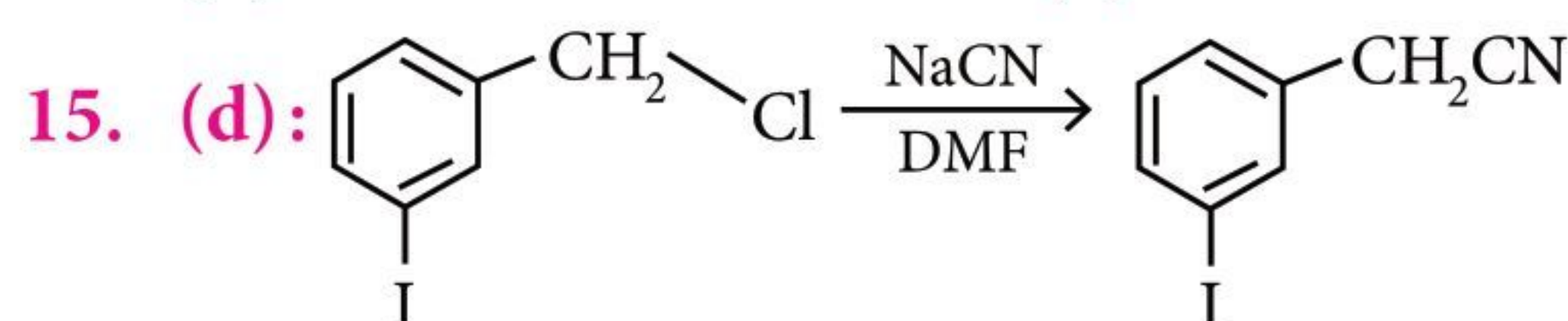
$$= \frac{3.996 \times (40 \text{ g mol}^{-1})}{(0.560 \times 10^{-7} \text{ cm})^3 \times (6.022 \times 10^{23} \text{ mol}^{-1})}$$

$$= 1.51 \text{ g cm}^{-3}$$



13. (d)

14. (d)





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Unit  
9

## Principles Related to Practical Chemistry

### PHYSICAL PRACTICAL CHEMISTRY

#### TITRIMETRIC EXERCISES

##### Volumetric Analysis

Volumetric analysis is a process by which the concentration or strength of a chemical substance is measured by measuring the volume of its solution taking part in a given chemical reaction. The main process of this analysis is called titration.

##### Titration

There are various types of titrations *viz.*, acid-base titration, oxidation-reduction titration, iodine titration, complexometric titration, etc.

##### Some Important Terms

- **Analyte or titre** : The substance being analysed.
- **Titrant** : The substance added to the analyte in a titration.
- **Equivalence point** : It is the point where reaction between two solutions is just complete or the point in a titration at which the quantity of titrant is exactly sufficient for stoichiometric reaction to be complete with the analyte. At this point there is a sudden change in a physical property, such as indicator colour, pH, conductivity, or absorbance. It is also known as **end point**.
- **Indicator** : A compound having a physical property (usually colour) that changes abruptly near the equivalence point of a chemical reaction is known as indicator. It indicates the attainment of end point.
- **Standard solution** : A solution whose concentration is known is called standard solution.
- **Standardization** : It is the process in which concentration of a reagent is determined by reaction with a known quantity of second reagent whose concentration is known.
- **Primary standard substance** : A reagent that is pure enough so that its standard solution can be prepared directly by dissolving a definite weight of it in a definite volume of solvent is known as primary standard, *e.g.*, crystalline oxalic acid, anhydrous  $\text{Na}_2\text{CO}_3$ , Mohr's salt, etc. It is stable and unaffected by air. It is neither hygroscopic nor deliquescent. It is highly soluble in water.
- **Secondary standard substance** : The substance or reagent whose standard solution cannot be prepared directly is called secondary standard, *e.g.*  $\text{KMnO}_4$ ,  $\text{NaOH}$ ,  $\text{KOH}$ , etc. These substances do not occur in pure state. They are not stable in air. They are either hygroscopic or deliquescent.

##### Law of Chemical Equivalence

It states that number of equivalents of a substance to be titrated, react with equal number of equivalents of the titrant.

$$\text{Number of equivalents} = \text{Normality (N)} \times \text{Volume (V)} \quad (\text{in L})$$

$$\text{Number of equivalents of titre} = \text{Number of equivalents of titrant}$$



$$N_1 V_1 = N_2 V_2$$

If volume is taken in mL

Then, number of milliequivalents (m.eq.)

= Normality  $\times$  Volume (in mL)

then also,  $N_1 V_1 = N_2 V_2$

The above equation is known as **normality equation**.

Similarly, molarity equation is also given but it is usually applicable for dilution of a solution.

$$M_1 V_1 = M_2 V_2$$

Normality = Molarity  $\times n$ , where  $n$  = valency factor

Thus,  $N_1 V_1 = N_2 V_2$  can be written as :

$$\text{or } M_1 V_1 n_1 = M_2 V_2 n_2 \text{ or } \frac{M_1 V_1}{M_2 V_2} = \frac{n_2}{n_1}$$

### Types of Titrations

Acid-Base Titrations

Redox Titrations

## ACID-BASE TITRATION

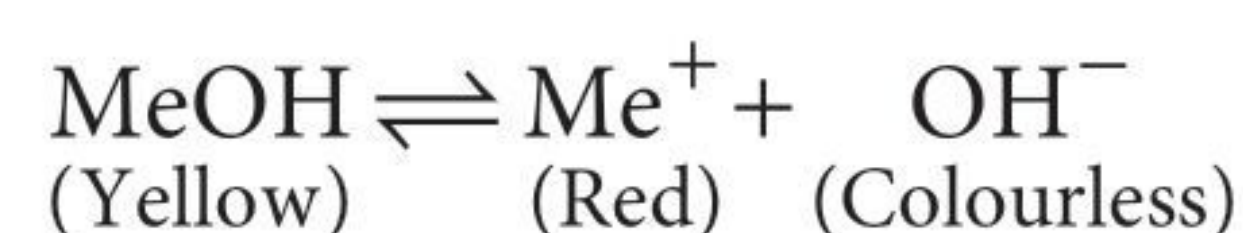
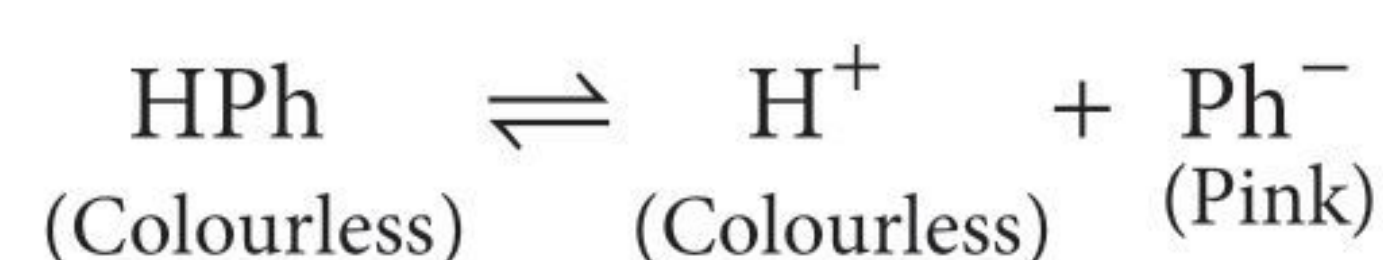
Acid-base titration involves neutralization reaction.



The point at which there is sudden change in pH with addition of very small amount of the titrant to the titrate (titre) is called **point of inflection** or end point.

### Indicator

Acid-base indicators are generally complex organic molecules which are either weak acids or weak bases, e.g., phenolphthalein is a weak organic acid (represented as HPh) and methyl orange is a weak organic base (represented as MeOH). These indicators dissociate in aqueous solution such that the unionised indicator and its conjugate part (*i.e.*, either conjugate acid or conjugate base) have different colours.



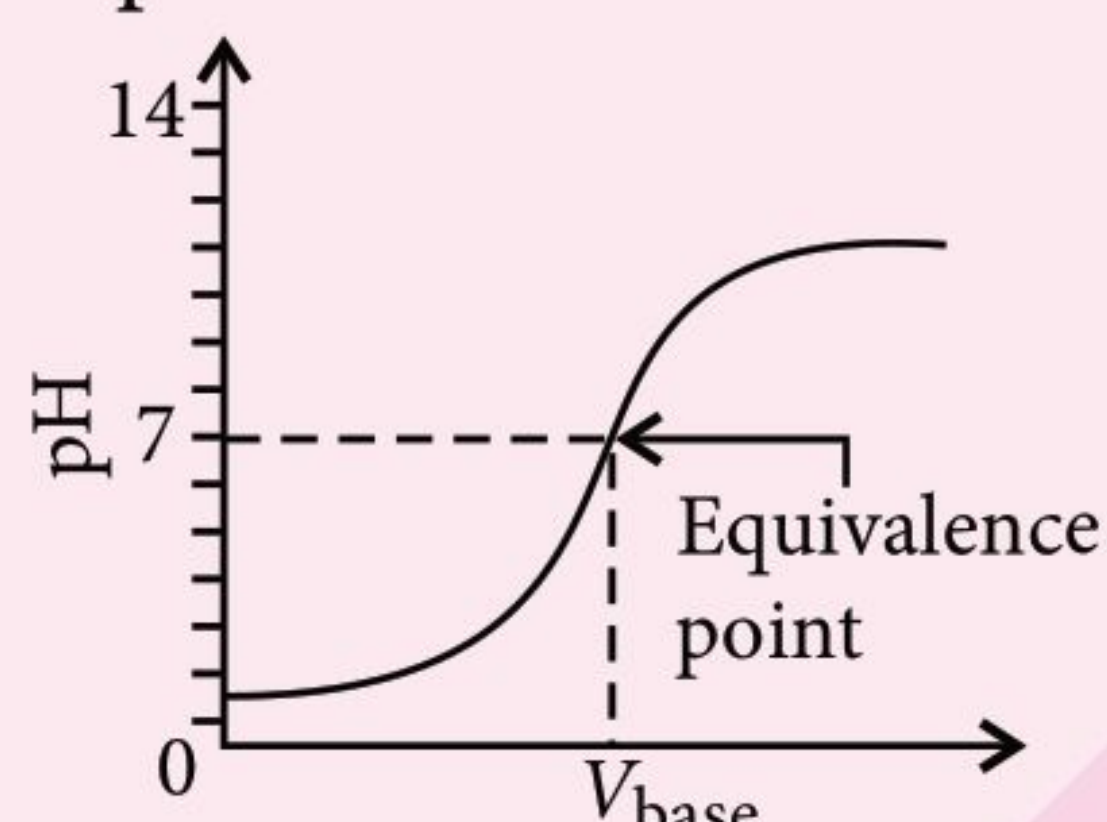
An indicator show change in colour in the same pH range as developed around the equivalence point.

### Some common acid-base indicators

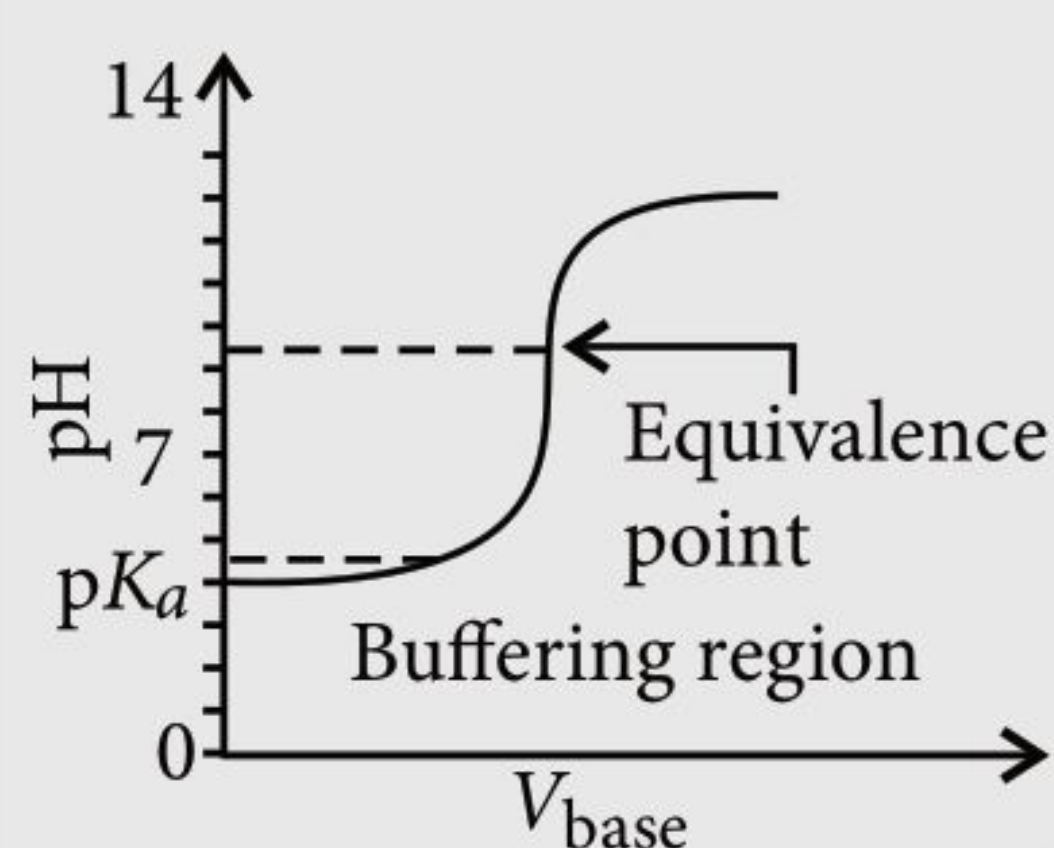
Indicator colour change, from acidic to alkaline medium	$pK_{\text{(ind)}}$	pH range	Example of titration
Methyl orange (red $\Rightarrow$ yellow)	3.7	3.1 – 4.4	Weak base vs strong acid titration
Methyl red (red $\Rightarrow$ yellow)	5.1	4.2 – 6.3	Weak base vs strong acid titration
Phenol red (yellow $\Rightarrow$ red)	7.9	6.4 – 8.2	Strong acid vs strong base titration
Phenolphthalein (colourless $\Rightarrow$ pink)	9.3	8.3 – 10.0	Weak acid vs strong base titration

### Acid-Base Titrations

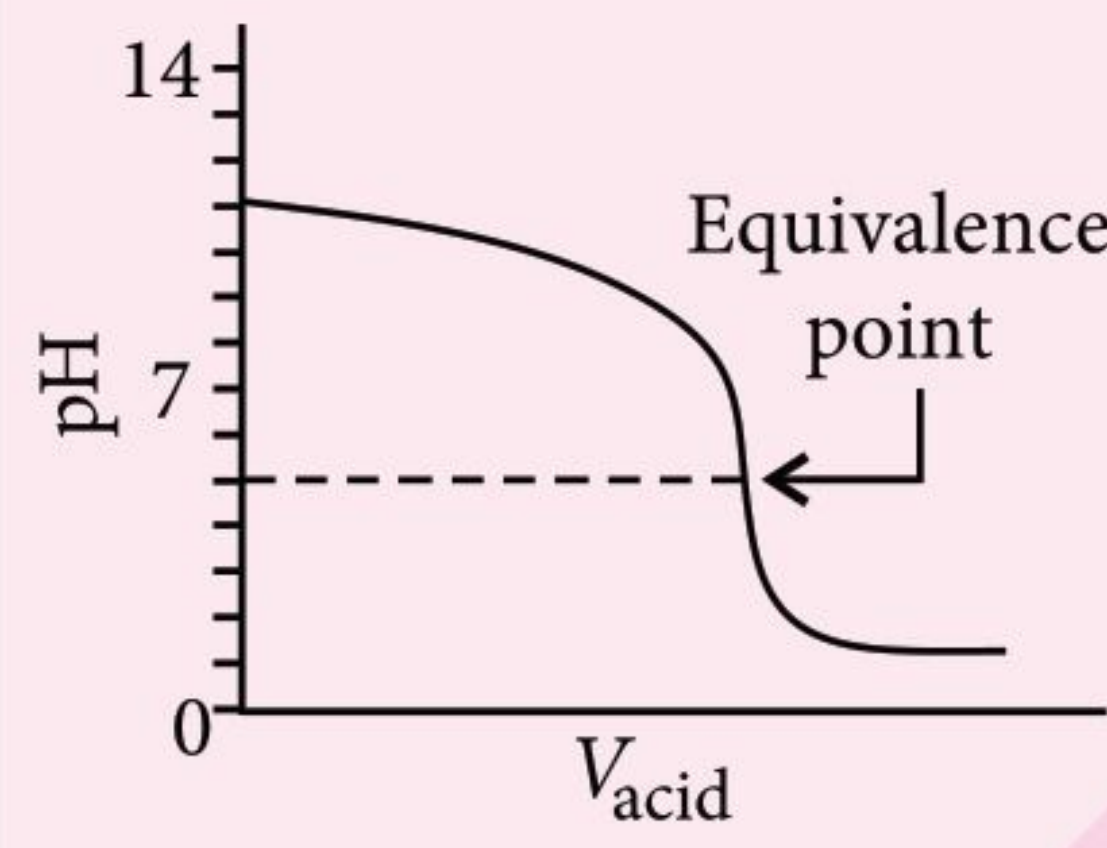
**Strong acid + strong base**  
(Salt does not undergo hydrolysis)  
Equivalence point at pH = 7



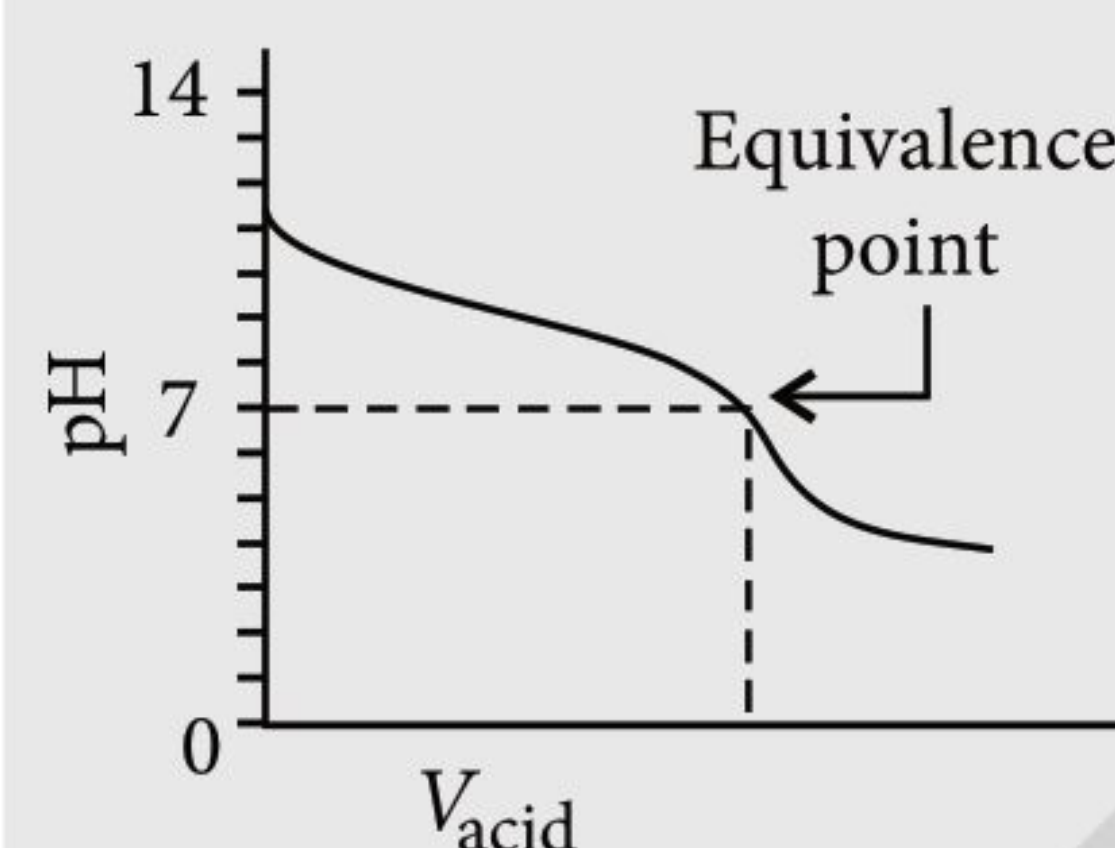
**Weak acid + strong base (Anionic hydrolysis)**  
Equivalence point at pH > 7



**Weak base + strong acid (Cationic hydrolysis)**  
Equivalence point at pH < 7



**Weak base + weak acid**  
(No sharp end point)  
Equivalence point at pH  $\approx$  7





## REDOX TITRATION

Redox titrations involving  $\text{KMnO}_4$  as oxidising agent are called **permanganometric titrations**. In these titrations reducing agents like Mohr's salt,  $((\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O})$ ,  $\text{FeSO}_4$ ,  $\text{H}_2\text{O}_2$ , oxalic acid and oxalates are directly titrated against  $\text{KMnO}_4$  as oxidising agent in acidic medium.

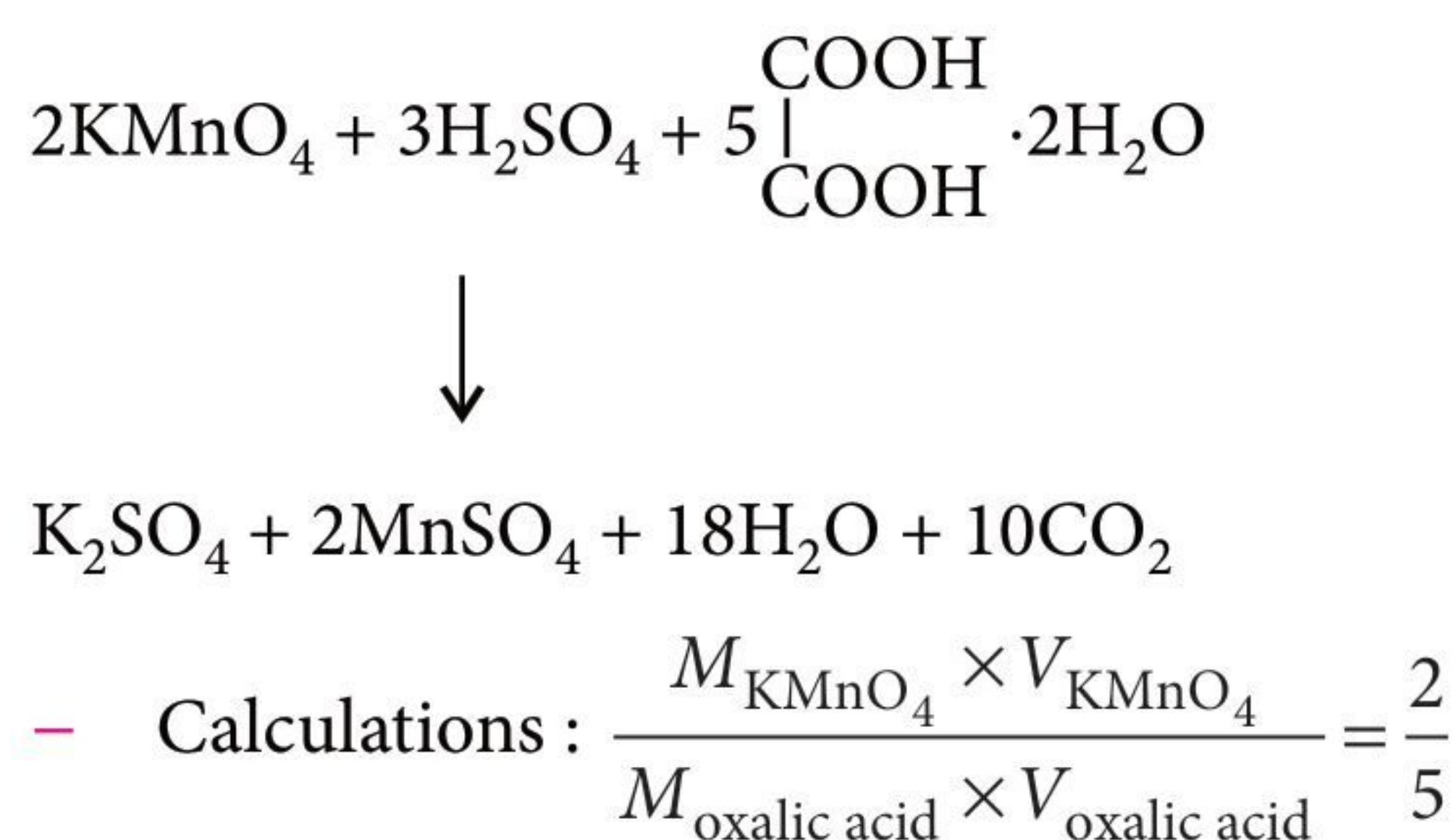
### Indicator

In these titrations,  $\text{KMnO}_4$  acts as self indicator. In acidic medium,  $\text{KMnO}_4$  reacts with reducing agent (like oxalic acid or Mohr's salt), when whole of the reducing agent has been oxidised the remaining  $\text{KMnO}_4$  is not decomposed and imparts pink colour to the solution and thus acts as an indicator.

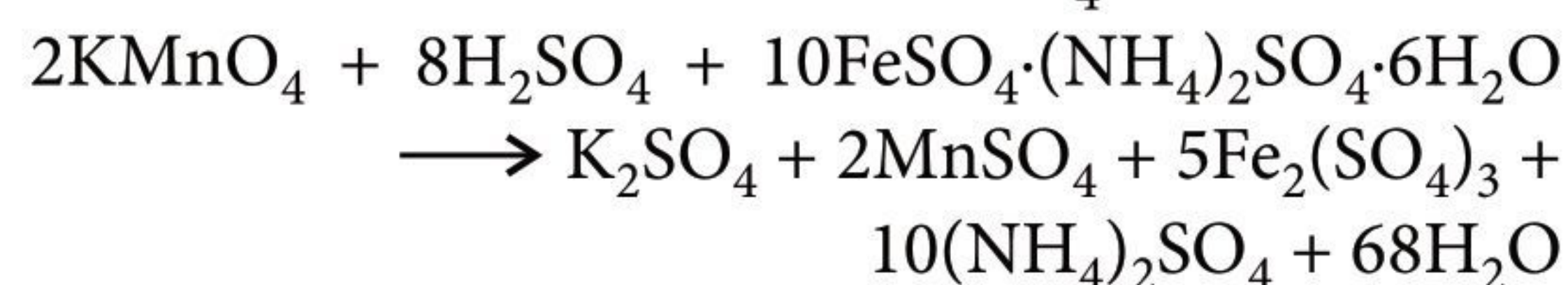
### End point

In  $\text{KMnO}_4$  titration end point is from colourless to permanent light pink colour.

- **Titration of oxalic acid vs  $\text{KMnO}_4$ :**



- **Titration of Mohr's salt vs  $\text{KMnO}_4$ :**



$$\text{Calculations : } \frac{M_{\text{KMnO}_4} \times V_{\text{KMnO}_4}}{M_{\text{Mohr's salt}} \times V_{\text{Mohr's salt}}} = \frac{1}{5}$$

## ORGANIC PRACTICAL CHEMISTRY

### DETECTION OF EXTRA ELEMENTS (N, S AND HALOGENS) IN ORGANIC COMPOUNDS

Carbon and hydrogen are present in almost all the organic compounds. Other commonly present elements are nitrogen, halogens and sulphur, which can be detected qualitatively by **Lassaigne's test**.

#### Preparation of Lassaigne's Extract

A small piece of sodium is heated gently in an ignition tube till the sodium melts. About 50 to 60 mg of the organic compound is added to this and the tube heated strongly for 2-3 minutes to fuse the material inside it. After cooling, the tube is carefully broken in a china dish containing about 20 to 30 mL of distilled water. The fused material along with the pieces of ignition tube is crushed with the help of a glass rod and the contents of the china dish are boiled for a few minutes. The sodium salts formed in the above reaction (*i.e.*,  $\text{NaCN}$ ,  $\text{Na}_2\text{S}$ ,  $\text{NaX}$  or  $\text{NaSCN}$ ) dissolve in water. Excess of sodium reacts with water to give sodium hydroxide. This alkaline solution is called Lassaigne's extract or sodium extract.

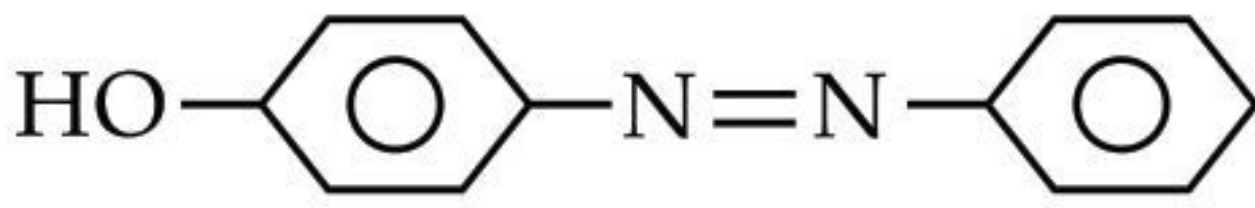
Element	Detection	Confirmatory test	Reactions
Nitrogen	Lassaigne's extract (L.E.) $\text{Na} + \text{C} + \text{N} \xrightarrow{\Delta} \text{NaCN}$ (L.E.)	L.E. + $\text{FeSO}_4$ + $\text{NaOH}$ , boil and cool + $\text{FeCl}_3$ + conc. $\text{HCl}$ Gives blue or green colour.	$\text{FeSO}_4 + 2\text{NaOH} \longrightarrow \text{Fe}(\text{OH})_2 + \text{Na}_2\text{SO}_4$ $\text{Fe}(\text{OH})_2 + 6\text{NaCN} \longrightarrow \text{Na}_4[\text{Fe}(\text{CN})_6] + 2\text{NaOH}$ $3\text{Na}_4[\text{Fe}(\text{CN})_6] + 4\text{FeCl}_3 \longrightarrow \text{Fe}_4[\text{Fe}(\text{CN})_6]_3 + 12\text{NaCl}$ Prussian blue
Sulphur	$2\text{Na} + \text{S} \xrightarrow{\Delta} \text{Na}_2\text{S}$ (L.E.)	(i) L.E. + sodium nitroprusside A deep violet colour. (ii) L.E. + $\text{CH}_3\text{COOH}$ + $(\text{CH}_3\text{COO})_2\text{Pb}$ Gives a black ppt.	(i) $\text{Na}_2\text{S} + \text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \longrightarrow$ Sodium nitroprusside $\text{Na}_4[\text{Fe}(\text{CN})_5\text{NOS}]$ Deep violet (ii) $\text{Na}_2\text{S} + (\text{CH}_3\text{COO})_2\text{Pb} \xrightarrow{\text{CH}_3\text{COOH}}$ $\text{PbS} \downarrow + 2\text{CH}_3\text{COONa}$ Black ppt.



Halogens	$\text{Na} + \text{X} \xrightarrow{\Delta} \text{NaX}$ (L.E.)	L.E. + $\text{HNO}_3 + \text{AgNO}_3$ (i) White ppt. soluble in aq. $\text{NH}_3$ (or $\text{NH}_4\text{OH}$ ) confirms Cl. (ii) Yellow ppt. partially soluble in aq. $\text{NH}_3$ (or $\text{NH}_4\text{OH}$ ) confirms Br. (iii) Yellow ppt. insoluble in aq. $\text{NH}_3$ (or $\text{NH}_4\text{OH}$ ) confirms I.	$\text{NaX} + \text{AgNO}_3 \xrightarrow{\text{HNO}_3} \text{AgX} \downarrow$ White ppt. $\text{AgCl} + 2\text{NH}_{3(aq.)} \longrightarrow [\text{Ag}(\text{NH}_3)_2]\text{Cl}$ Soluble
Nitrogen and sulphur together	$\text{Na} + \text{C} + \text{N} + \text{S} \xrightarrow{\Delta} \text{NaSCN}$ (L.E.)	As in test for nitrogen; instead of green or blue colour, blood red colouration confirms presence of N and S both.	$3\text{NaSCN} + \text{FeCl}_3 \longrightarrow \text{Fe}(\text{SCN})_3$ Blood red colour + $3\text{NaCl}$

## DETECTION OF FUNCTIONAL GROUP

- An atom or group of atoms that largely determines the properties of an organic compound is called functional group.

Test		Reaction	Confirmation
<b>(A) Detection of unsaturation</b>			
(i)	Baeyer's or $\text{KMnO}_4$ test	$2\text{KMnO}_4 + \text{H}_2\text{O} \longrightarrow 2\text{KOH} + 2\text{MnO}_2 + 3[\text{O}]$ $>\text{C}=\text{C}< + \text{H}_2\text{O} + [\text{O}] \longrightarrow \begin{array}{c} >\text{C}-\text{C}< \\   \quad   \\ \text{OH} \quad \text{OH} \end{array}$	Disappearance of pink colour of $\text{KMnO}_4$ .
(ii)	$\text{Br}_2 - \text{CCl}_4$ test	$>\text{C}=\text{C}< + \text{Br}_2 \xrightarrow[\text{Red brown}]{\text{CCl}_4} \begin{array}{c} \text{Br} \\   \\ >\text{C}-\text{C}< \\   \\ \text{Br} \end{array}$	Disappearance of brown colour.
<b>(B) Detection of alcoholic group</b>			
(i)	Acetyl chloride test	$\text{R}-\text{OH} + \text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{Cl} \longrightarrow \text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{R} + \text{HCl} \uparrow$	Evolution of $\text{HCl}$ gas and fruity smell.
(ii)	Ceric ammonium nitrate test	$2\text{ROH} + (\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6] \longrightarrow [(\text{ROH})_2\text{Ce}(\text{NO}_3)_4] + 2\text{NH}_4\text{NO}_3$ Pink or red	Appearance of pink or red colour.
<b>(C) Detection of phenolic group</b>			
(i)	$\text{FeCl}_3$ test	$\text{FeCl}_3 + 6\text{C}_6\text{H}_5\text{OH} \longrightarrow [\text{Fe}(\text{OC}_6\text{H}_5)_6]^{3-} + 3\text{H}^+ + 3\text{HCl}$ Violet	Appearance of violet colouration.
(ii)	Azo dye test	$\text{C}_6\text{H}_5\text{NH}_2 + \text{NaNO}_2 + \text{HCl} \longrightarrow \text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^-$ $\text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^- + \text{C}_6\text{H}_5\text{OH} \xrightarrow[0-5^\circ\text{C}]{\text{pH } 9-10}$  <i>p</i> -Hydroxyazobenzene (orange)	Formation of orange or red dye.



**(D) Detection of carbonyl group**

<b>Aldehydic/Ketonic group</b>			
(i)	Brady's reagent (2, 4-DNP) test	$\text{>C=O} + \text{H}_2\text{NNH}-\text{C}_6\text{H}_3(\text{NO}_2)_2 \xrightarrow{\text{2,4-Dinitrophenylhydrazine}}$ $\text{>C=NNH}-\text{C}_6\text{H}_3(\text{NO}_2)_2$ <p>Yellow, orange or red ppt.</p>	Appearance of yellow, orange or red ppt.
(ii)	Sod. bisulphite test	$\text{>C=O} + \text{NaHSO}_3 \longrightarrow \text{>C} \begin{matrix} \text{OH} \\ \text{SO}_3^- \text{Na}^+ \end{matrix}$ <p>White ppt.</p>	Appearance of white ppt.

**Aldehydic group**

(i)	Tollens' test	$\text{RCHO} + 2[\text{Ag}(\text{NH}_3)_2]\text{OH} \longrightarrow \text{RCOONH}_4 + 3\text{NH}_3 + \text{H}_2\text{O} + 2\text{Ag}_{(s)} \downarrow$ <p>(Silver mirror)</p>	Formation of silver mirror along the sides of the test tube.
(ii)	Fehling's test	$\text{RCHO} + 2\text{Cu}^{2+} + 3\text{OH}^- \longrightarrow 2\text{Cu}^+ \downarrow + \text{RCOO}^- + 2\text{H}_2\text{O}$ <p>Red ppt.</p>	A red ppt. is formed (only by aliphatic aldehydes).
(iii)	Benedict's test	$\text{RCHO} + 2\text{Cu}(\text{OH})_2 + \text{NaOH} \longrightarrow \text{RCOONa} + \text{Cu}_2\text{O} \downarrow + 3\text{H}_2\text{O}$ <p>Red ppt.</p>	Appearance of red ppt.

**Ketonic group**

(i)	Iodoform test	$\text{R}-\text{CO}-\text{CH}_3 + 3\text{I}_2 + 4\text{NaOH} \longrightarrow 3\text{NaI} + \text{CHI}_3 \downarrow + \text{RCOONa} + 3\text{H}_2\text{O}$ <p>Yellow ppt.</p>	Formation of yellow ppt. of $\text{CHI}_3$ (for methyl ketones only).
(ii)	Sodium nitroprusside test	$\text{RCOR} + \text{sod. nitroprusside solution} + \text{NaOH} \longrightarrow \text{Wine-red coloured complex}$	Appearance of wine-red colour.

**(E) Detection of carboxylic group**

(i)	$\text{NaHCO}_3$ test	$\text{RCOOH} + \text{NaHCO}_3 \longrightarrow \text{RCOONa} + \text{H}_2\text{O} + \text{CO}_2 \uparrow$	Brisk effervescence of $\text{CO}_2$ indicates $-\text{COOH}$ group.
(ii)	Ester test	$\text{RCOOH} + \text{C}_2\text{H}_5\text{OH} \xrightarrow[\Delta]{\text{Conc. H}_2\text{SO}_4} \text{RCOOC}_2\text{H}_5 + \text{H}_2\text{O}$	Fruity smell of esters formed.
(iii)	$\text{FeCl}_3$ test	$3\text{RCOOH} + 3\text{NH}_4\text{OH} + \text{FeCl}_3 \longrightarrow (\text{RCOO})_3\text{Fe} + 3\text{NH}_4\text{Cl} + 3\text{H}_2\text{O}$ $\downarrow \text{H}_2\text{O}$ $\text{Fe}(\text{OH})(\text{OOCR})_2 + \text{RCOOH}$ <p>Basic iron salt</p>	Red : acetic acid, formic acid No colour change : oxalic acid Violet : salicylic acid Buff : benzoic acid

**(F) Detection of amino group****Primary amines**

(i)	Carbylamine test	$\text{R}-\text{NH}_2 + \text{CHCl}_3 + 3\text{KOH} \xrightarrow{\Delta} \text{R}-\text{N} \equiv \text{C} + 3\text{KCl} + 3\text{H}_2\text{O}$ <p>Isocyanide</p>	Offensive smell of isocyanide indicates $1^\circ$ aliphatic or aromatic amino group.
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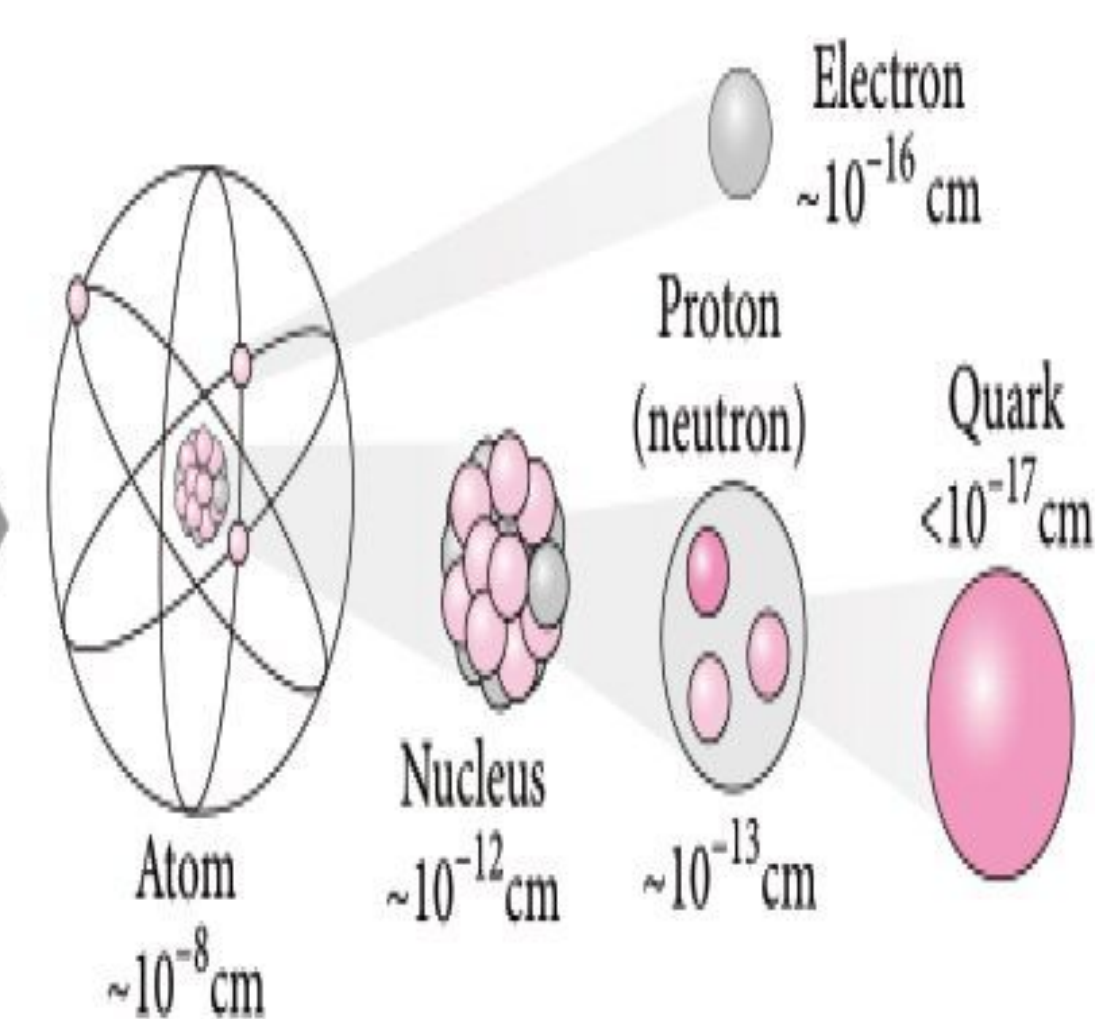
# CONCEPT MAP

## STRUCTURE OF ATOM

Niels Henrik David Bohr (Niels Bohr), a Danish physicist who is generally regarded as one of the foremost physicists of the 20th century. He was the first to apply the quantum concept, to the problem of atomic and molecular structure. For that work he received the Nobel Prize in Physics in 1922. His manifold roles in the origins and development of quantum physics is his most important contribution.



### FUNDAMENTAL PARTICLES



### QUANTUM NUMBERS

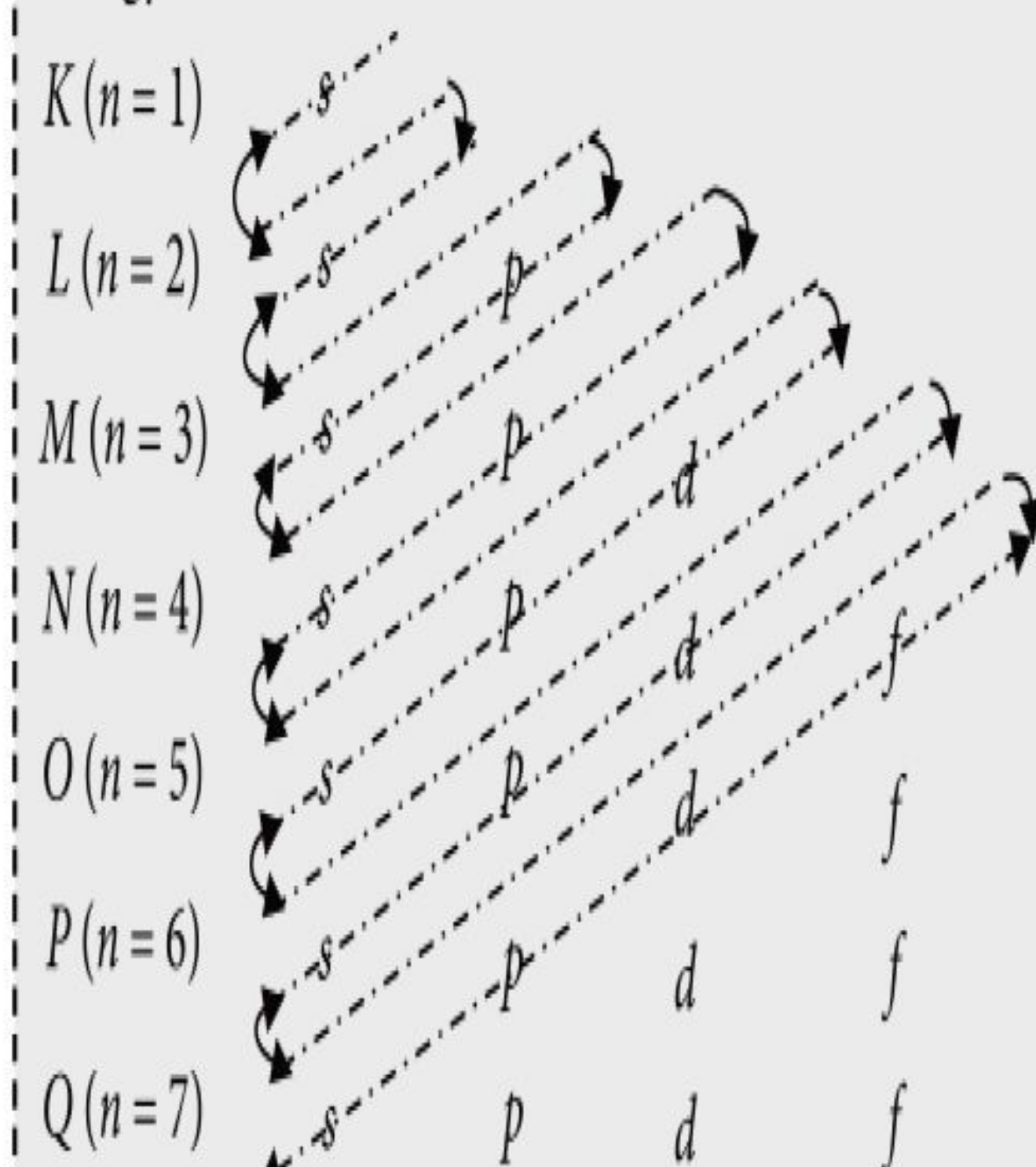
A set of four members which helps to determine the complete information about all the  $e^-$  in an atom.

Symbol	Quantum Numbers	Values	Role
$n$	Principal	1, 2, 3, ....	Determines the energy (size).
$l$	Angular	0, 1, 2, .... $n - 1$	Special distribution of electron cloud and angular momentum.
$m_l$	Magnetic	0, $\pm 1$ , $\pm 2$ , .... $\pm l$	Determines the orientation in space.
$m_s$	Spin	$\pm 1/2$	Describes the electron spin (magnetic moment).

### Rules for Assigning Electrons

- **Aufbau principle**:  $e^-$  occupy lowest energy orbital available.
- **Pauli exclusion principle**: Maximum 2 electrons per orbital must have opposite spins.
- **Hund's rule**: If two or more orbitals of equal energy are available, electrons will occupy them singly before filling in pairs.

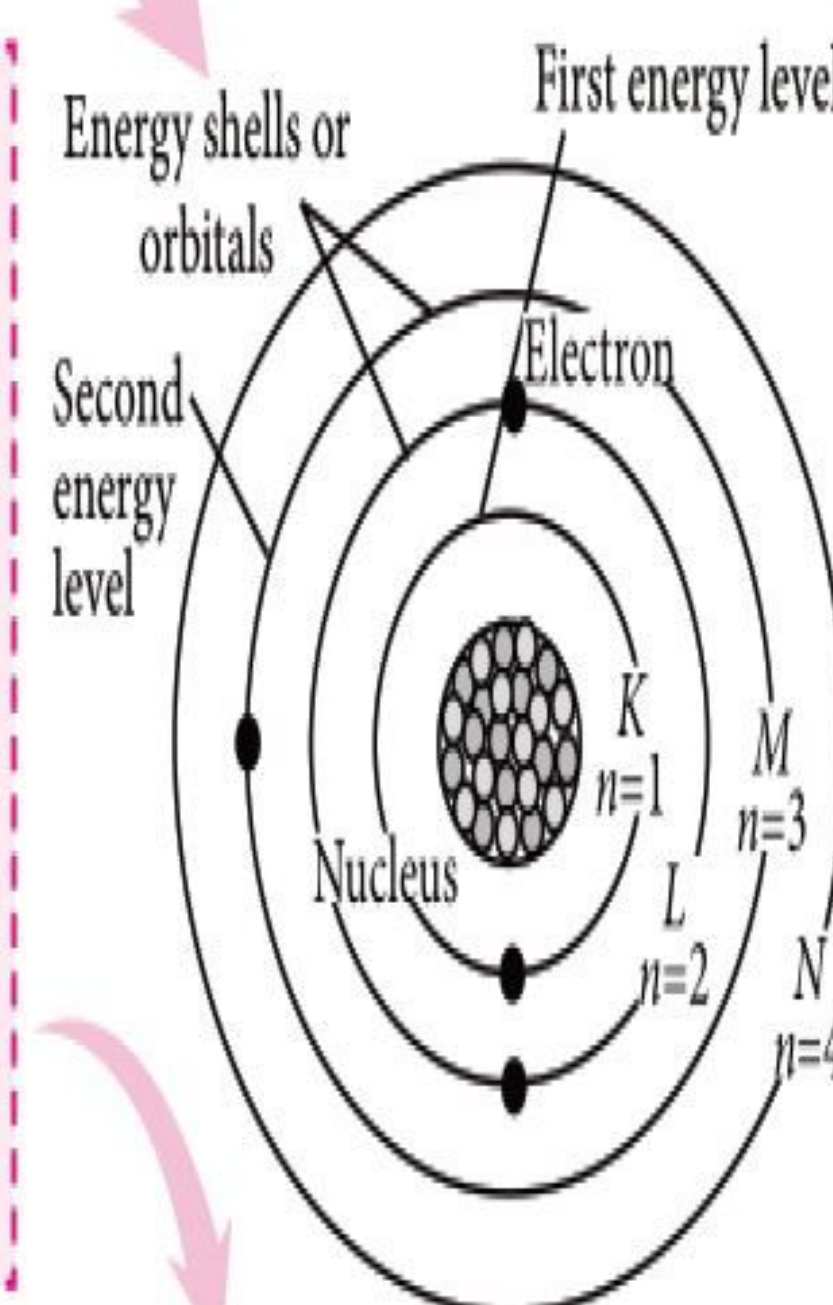
### Energy Level



$l$	0	1	2	3
Sub-shell	s	p	d	f
Orbital present	1	3	5	7

### Bohr's Model

- An atom consists of a small heavy positively charged nucleus.
- The electrons revolve only in those orbits which have a fixed value of energy.



### Hydrogen Spectrum

According to Bohr's theory, an electron neither emits nor absorbs energy as long as it stays in a particular orbit.

However, an electron in an atom may jump from normal energy level, to some higher energy level. During each such jump, energy is emitted in the form of a photon ( $h\nu$ ).

$$E_2 - E_1 = h\nu = hc/\lambda$$

Different excited electrons adopt different routes to return to various lower energy levels.

Lyman series : From  $n = 2, 3, 4, \dots$  to  $n = 1$

Balmer series : From  $n = 3, 4, 5, \dots$  to  $n = 2$

Paschen series : From  $n = 4, 5, 6, \dots$  to  $n = 3$

Brackett series : From  $n = 5, 6, 7, \dots$  to  $n = 4$

Pfund series : From  $n = 6, 7, 8, \dots$  to  $n = 5$

### Towards Quantum Mechanical Model

- **Dual nature of matter**: Every material particle in motion has dual nature (particle and wave nature).

$$\text{de-Broglie wavelength, } \lambda = \frac{h}{mv} = \frac{h}{p}$$

- **Heisenberg's uncertainty principle**: It is impossible to measure simultaneously the exact position and momentum of an electron.

$$\Delta x \times \Delta p \geq \frac{h}{4\pi}$$

### Quantum Mechanical Model

- The electrons in an atom have only quantized values of energy.
- These quantized values of energy are obtained from the solution of Schrodinger wave equation.

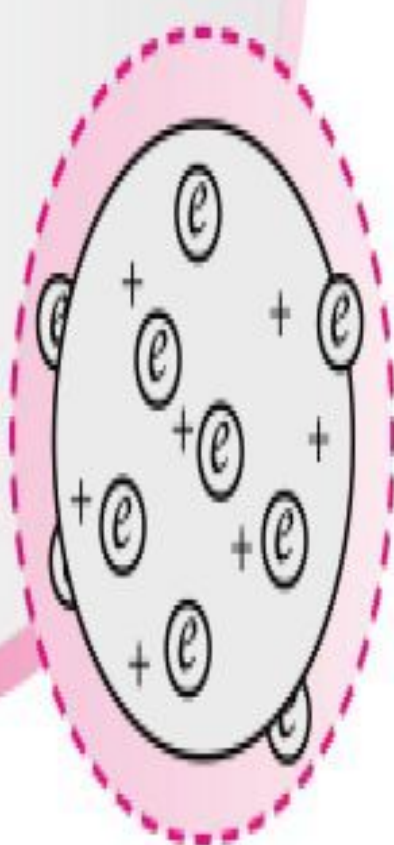
$$\frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} + \frac{d^2\psi}{dz^2} + \frac{8\pi^2m}{h^2}(E - V)\psi = 0$$

By finding  $\psi^2$  at different points around the nucleus in an atom, we can predict the region of space around the nucleus within which the probability of finding the electron is maximum.

### ATOMIC MODELS

#### Thomson's Model (1904)

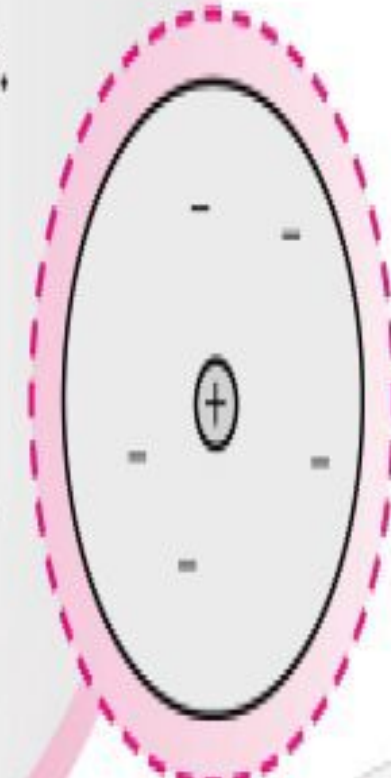
- Plum pudding model
- An atom was a sphere of positive charge in which number of electrons were embedded, sufficient to neutralize the positive charge.



#### Rutherford's Model (1911)

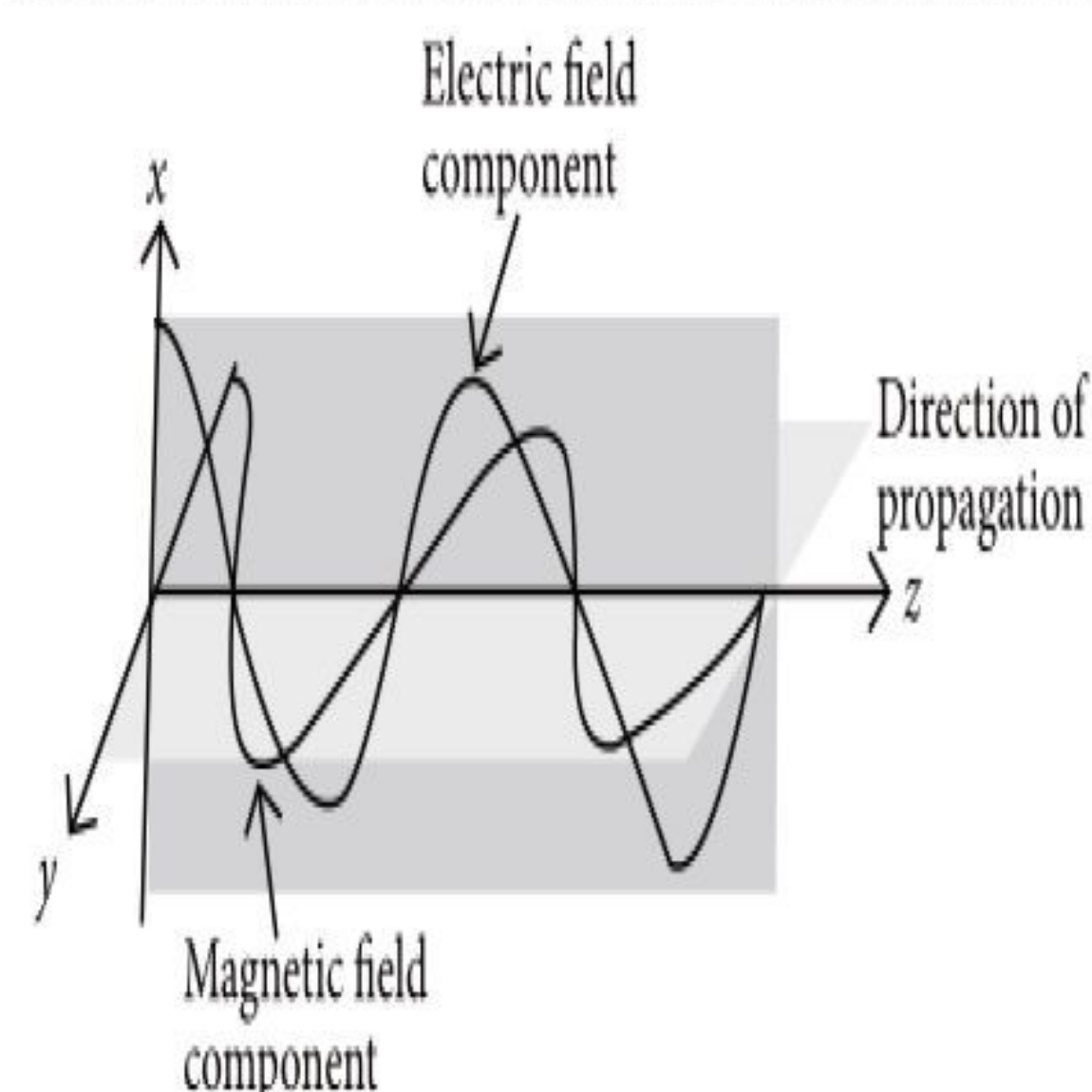
The atom consists of two parts:

- **Nucleus**: Very small in size, carries positive charge.
- **Extra-nuclear part, i.e., orbit**: Space around the nucleus in which electrons were distributed.

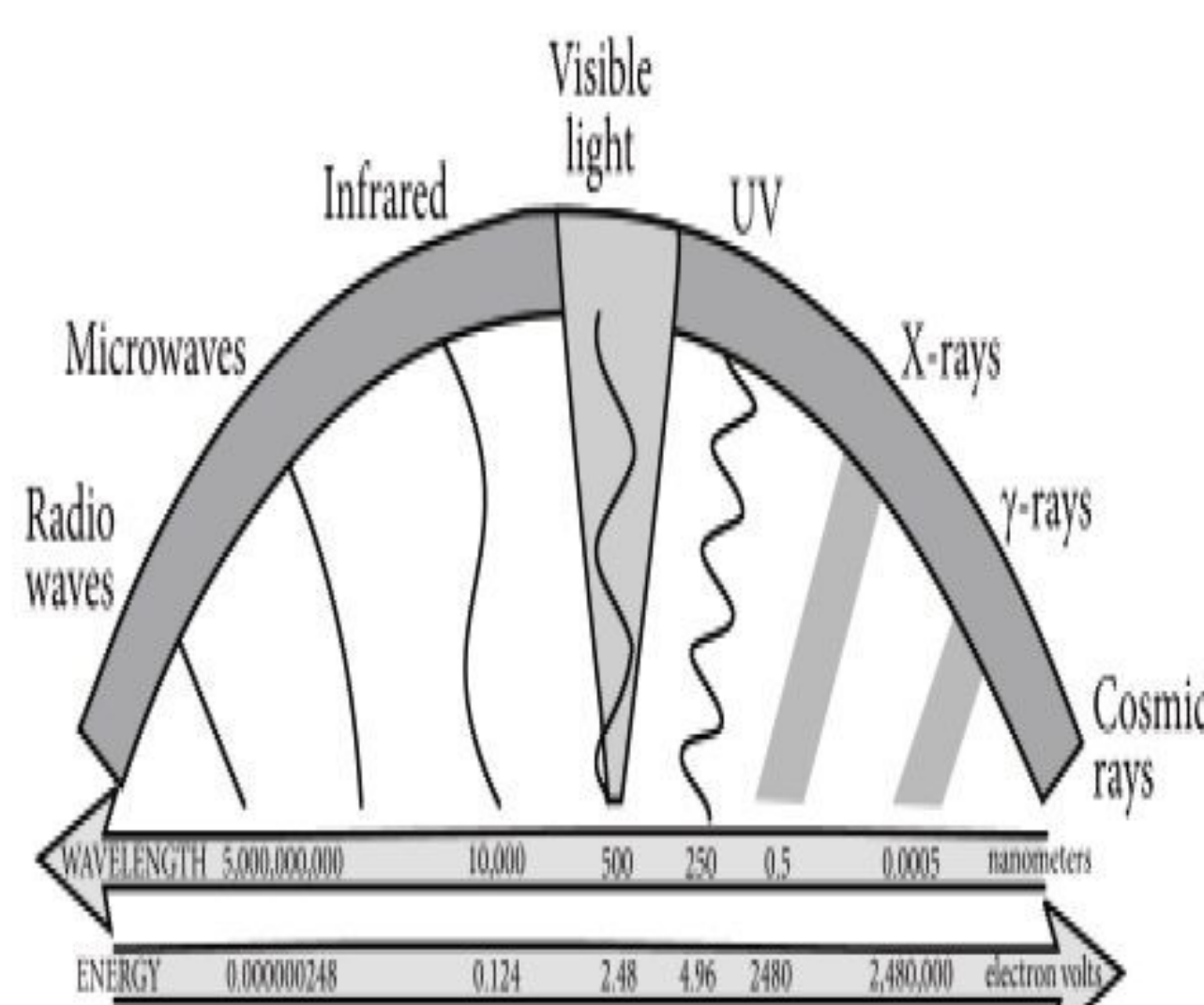


### Electromagnetic Wave Theory

- James Maxwell (1870) suggested that when electrically charged particles move under acceleration, alternating electrical and magnetic fields are produced and transmitted. These fields are transmitted in the forms of waves, called electromagnetic waves or electromagnetic radiations.



- **Electromagnetic Spectrum**: The electromagnetic spectrum is a continuum of all electromagnetic waves arranged according to frequency and wavelength. Cosmic rays <  $\gamma$ -rays < X-rays < Ultra-violet rays < Visible < Infrared < Microwaves < Radio waves



### Particle Nature of Electromagnetic Radiations

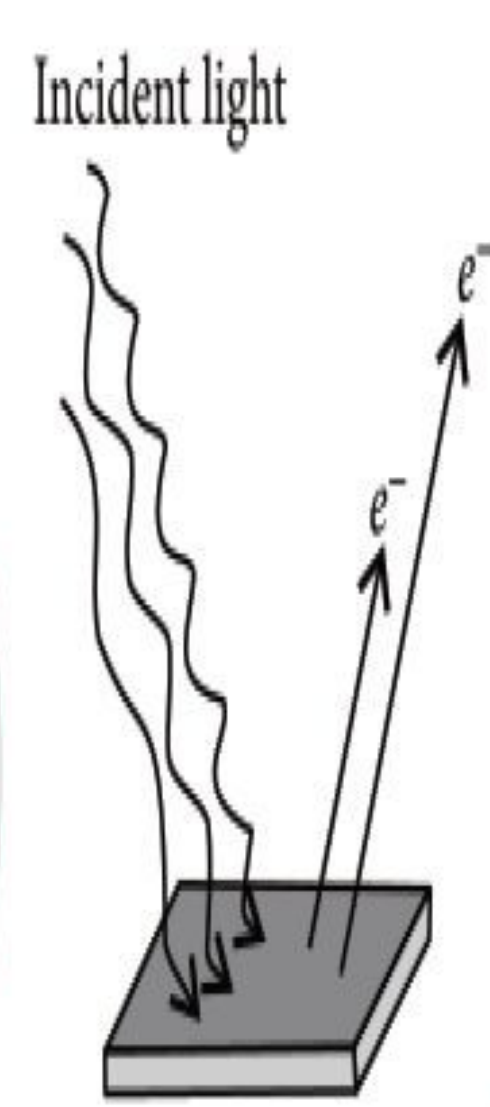
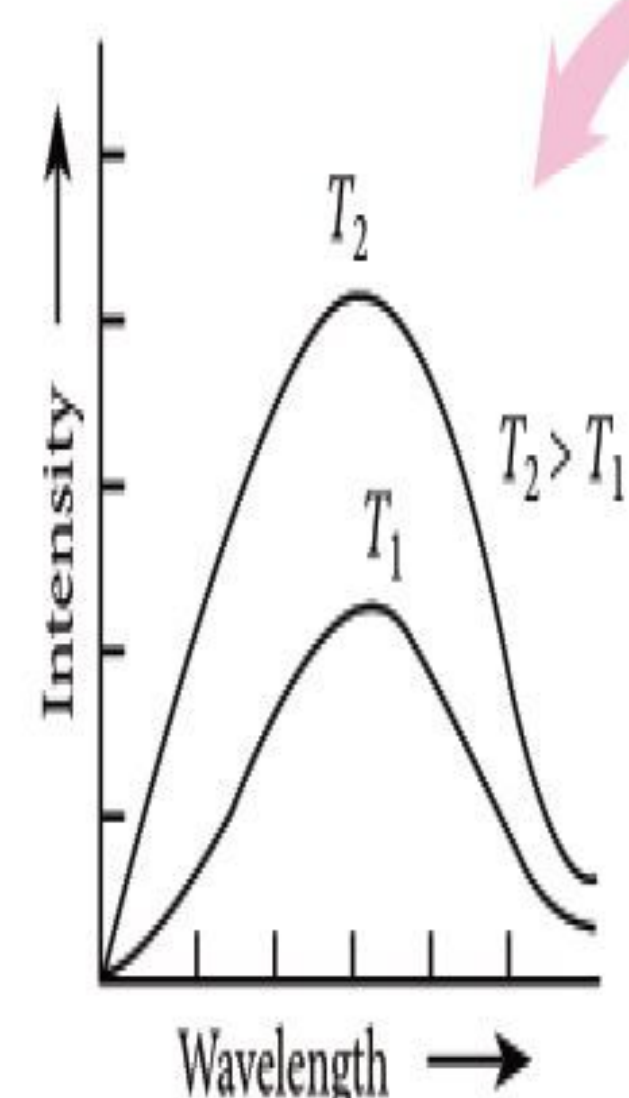
- **Planck's Quantum Theory**: A body can emit or absorb energy only in terms of integral multiple of a quantum/photon.

$$E = nh\nu;$$

where,  $n = 1, 2, 3, \dots$

### Black Body Radiation

If the substance being heated is a black body (which can emit and absorb all frequencies), the radiation emitted is called black body radiation.



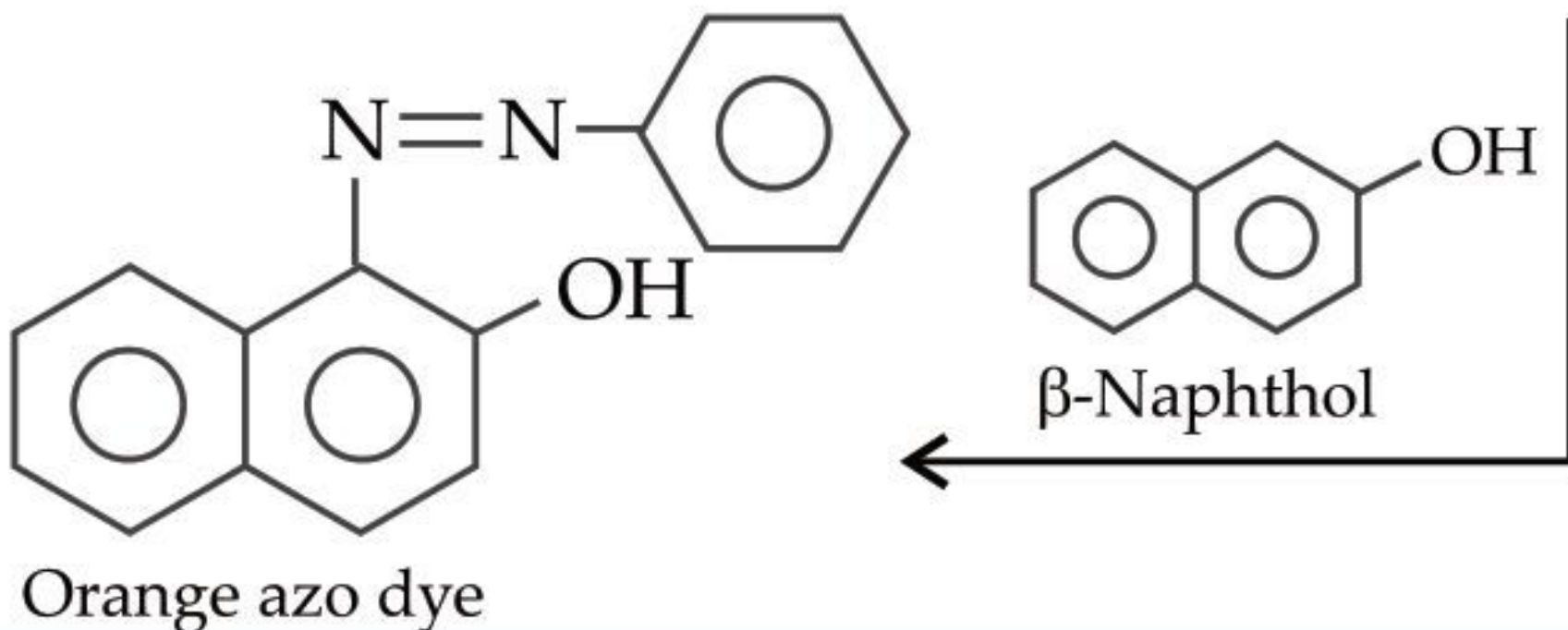
### Photoelectric Effect

When radiations with frequency greater than a certain minimum frequency ( $\nu_0$ ) strike the surface of a metal, the electrons are ejected from the surface of the metal. This phenomenon is called photoelectric effect.


$$E_{\text{photon}} = h\nu$$

$$E_{\text{K.E.}} = 1/2mv^2 = h\nu - h\nu_0$$

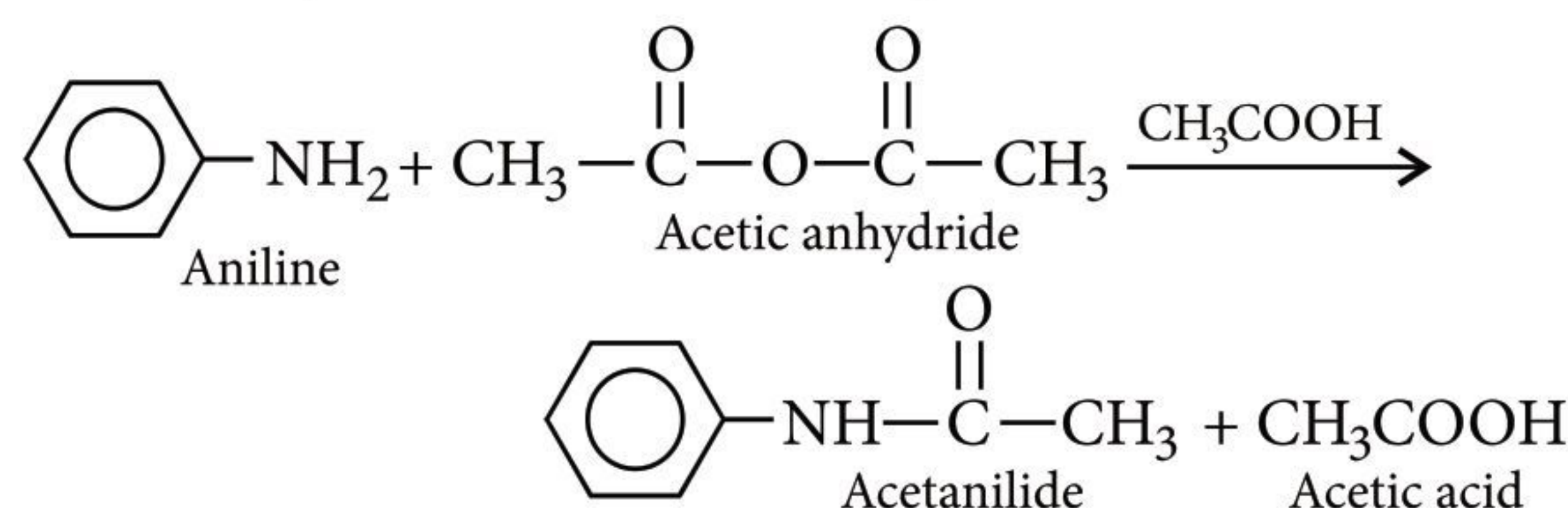


(ii)	Azo dye test	$\text{C}_6\text{H}_5\text{NH}_2 + \text{NaNO}_2 + \text{HCl} \xrightarrow[5-10 \text{ atm}]{0-5^\circ\text{C}} \text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^-$  <p>Orange azo dye</p>	A red or orange coloured dye confirms 1° aromatic amino group.
<b>Secondary amines</b>			
	Liebermann's nitroso test	$\text{C}_6\text{H}_5 - \underset{\text{CH}_3}{\text{N}} - \text{H} + \text{HNO}_2 \longrightarrow \text{C}_6\text{H}_5 - \underset{\text{CH}_3}{\text{N}} - \text{N} = \text{O} + \text{H}_2\text{O}$ <p style="text-align: center;">Nitrosoamine</p>	Formation of a yellow oily nitrosoamine indicates 2° aliphatic or aromatic amino group.
<b>(G) Detection of nitro group</b>			
(i)	Mulliken Barker test	$\text{RNO}_2 + 4[\text{H}] \xrightarrow{\text{Zn} + \text{NH}_4\text{Cl}} \text{RNHOH} + \text{H}_2\text{O}$ $\text{RNHOH} + 2[\text{Ag}(\text{NH}_3)_2]\text{OH} \longrightarrow \text{RNO} + 2\text{H}_2\text{O} + 4\text{NH}_3 + 2\text{Ag}\downarrow$ <p style="text-align: center;">Grey-black ppt.</p>	Appearance of grey-black ppt.
(ii)	Ferrous hydroxide test	$\text{RNO}_2 + 6\text{Fe}(\text{OH})_2 + 4\text{H}_2\text{O} \longrightarrow \text{RNH}_2 + 6\text{Fe}(\text{OH})_3\downarrow$ <p style="text-align: center;">Light green                      Brown ppt.</p>	Appearance of brown ppt.

## PREPARATION OF FEW ORGANIC COMPOUNDS

Acetanilide (*N*-Phenylethanamide): 

## Theory of experiment



Acetanilide is a useful intermediate in various reactions of aniline in which it protects the amino group.

***p*-Nitroacetanilide**

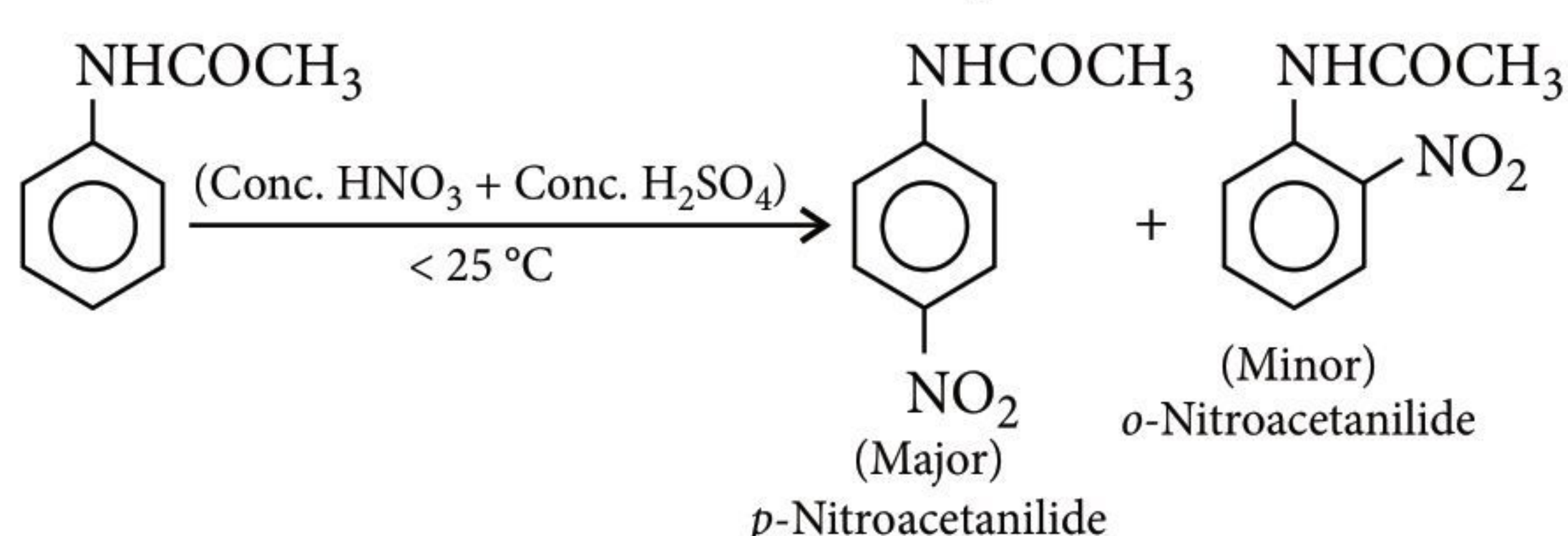
*p*-Nitroacetanilide is prepared by nitration of acetanilide. Powdered acetanilide is mixed with some amount of glacial acetic acid and concentrated  $\text{H}_2\text{SO}_4$  and mixture is cooled to a temperature less than  $5^\circ\text{C}$ . Now nitrating mixture (concentrated  $\text{HNO}_3$  + concentrated  $\text{H}_2\text{SO}_4$ ) is added to the reaction mixture with constant stirring, in such a way that temperature should not rise above  $25^\circ\text{C}$ . Pouring the content of



reaction mixture in crushed ice, separate the crude product. Pure product is obtained by recrystallisation of crude product in ethanol so that more soluble *o*-nitroacetanilide remains in mother liquor while *p*-nitroacetanilide is obtained as colourless crystals.

## Chemistry of experiment

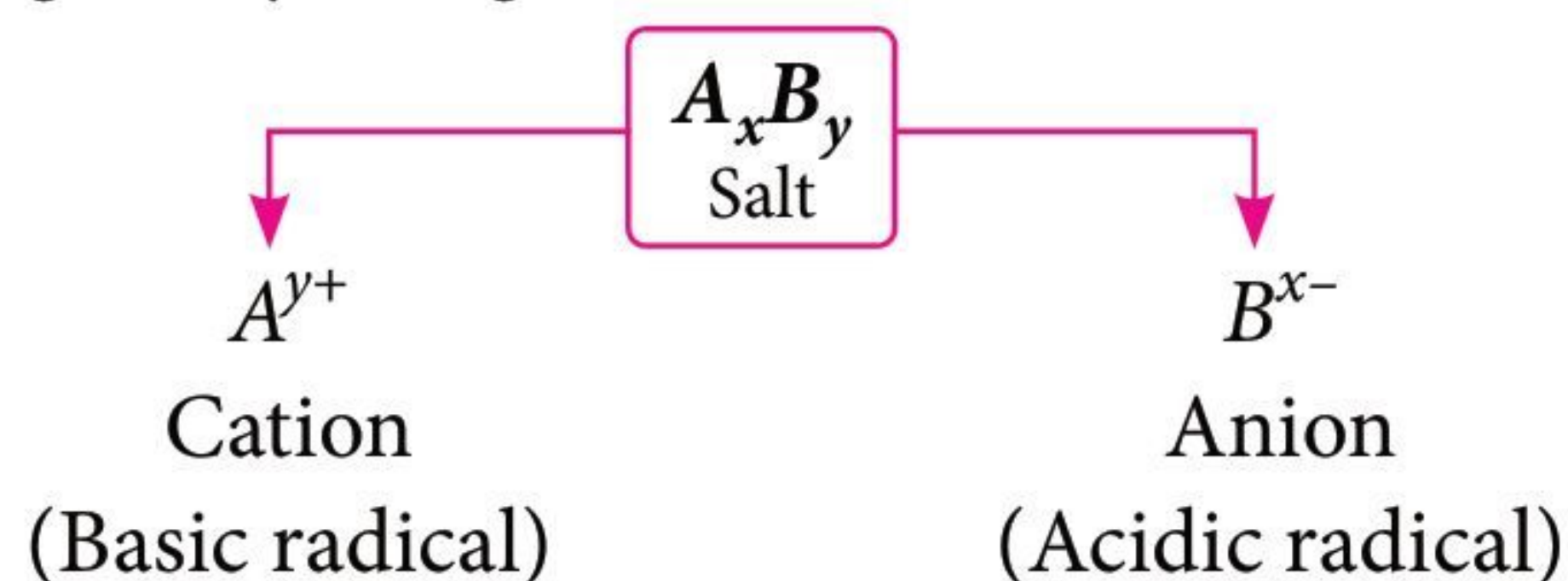
Direct nitration of aniline with nitric acid is not possible since nitric acid is a strong oxidising agent and it oxidises  $-NH_2$  group of aniline. So aniline is first acetylated to form acetanilide so that  $-NH_2$  group gets protected and then nitration is carried out with nitrating mixture in which *p*-nitroacetanilide is obtained as major product while *o*-nitroacetanilide as minor product.



# INORGANIC PRACTICAL CHEMISTRY

## QUALITATIVE ANALYSIS

- Qualitative analysis deals with the identification of various constituents present in a given compound. This analysis involves preliminary tests, flame test, wet tests for anions and cations etc.
- In the salt,  $A_xB_y$ ,  $A$  is positively charged ion and  $B$  is negatively charged ion.



## Dry Tests

### (a) Action of heat

A small amount of the salt is taken in an ignition tube and heated in a bunsen flame, first gently and then strongly. As a result, there occurs a change in the colour of the salts. A few examples have been listed below :

	Salt	Colour in cold	Colour in hot
1.	PbO	Light buff	Red
2.	Pb <sub>3</sub> O <sub>4</sub>	Red	Chocolate
3.	CuCl <sub>2</sub>	Blue	Brown
4.	CuSO <sub>4</sub>	Blue	White

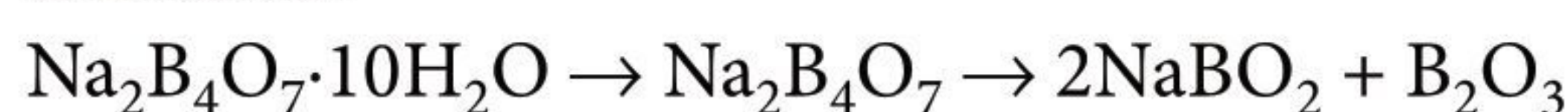
### (b) Flame test

Salt along with 1 to 2 drops of conc. HCl is taken and heated in the oxidising part of the flame using Pt wire. The presence of certain basic radicals imparts a characteristic colour to the flame.

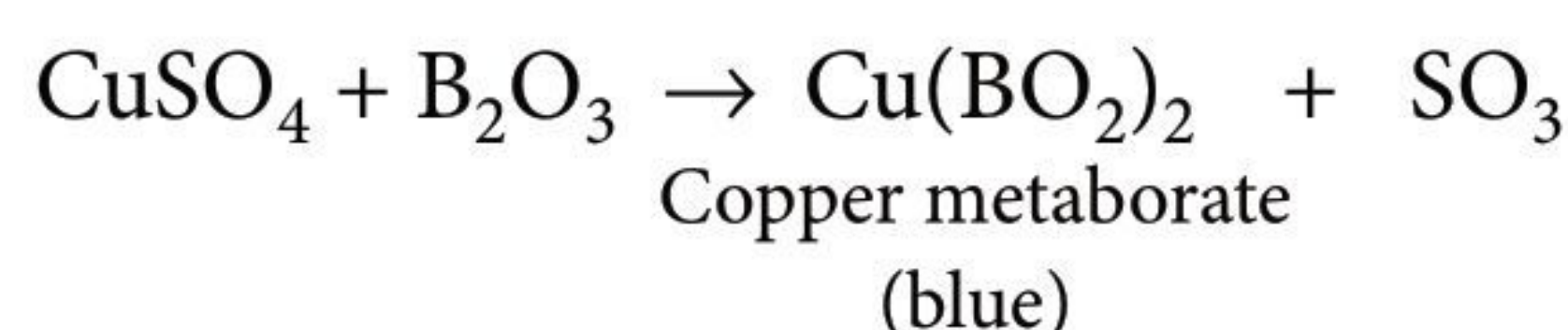
	Observation	Caused by
1.	Golden yellow	Na <sup>+</sup>
2.	Lilac	K <sup>+</sup>
3.	Brick red	Ca <sup>2+</sup>
4.	Apple green	Ba <sup>2+</sup>

### (c) Borax bead test

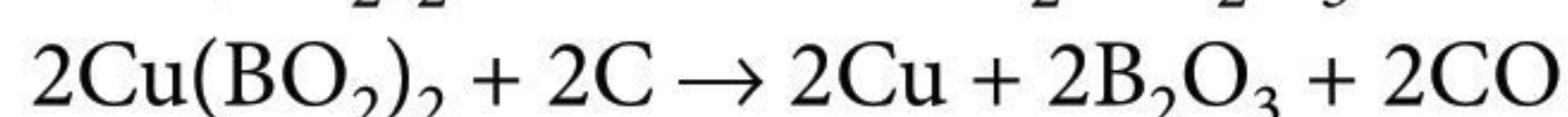
Borax is heated on a loop of Pt wire when colourless glassy bead of sodium metaborate and boric anhydride is formed.



Coloured salts are then heated on the glassy bead when coloured metaborate is formed in the oxidising flame.



In reducing flame we have



Hence, different colours appear in different flames.

Metal	Colour in			
	Oxidising flame		Reducing flame	
	Hot	Cold	Hot	Cold
Copper	Green	Blue	Colourless	Brown red
Iron	Brown-yellow	Pale yellow	Bottle green	Bottle green
Chromium	Green	Green	Green	Green
Cobalt	Blue	Blue	Blue	Blue
Manganese	Violet	Amethyst red	Grey	Grey
Nickel	Violet	Brown	Grey	Grey

## Wet Tests

### (a) Identification of acid radicals

- First group of acid radicals :** The acid radicals involved in this group are carbonate ( $\text{CO}_3^{2-}$ ), sulphide ( $\text{S}^{2-}$ ), sulphite ( $\text{SO}_3^{2-}$ ) and nitrite ( $\text{NO}_2^-$ ). The group reagent is dilute sulphuric acid.



Gas	Radical (Inference)	Confirmatory tests
CO <sub>2</sub> (Brisk effervescence of colourless, odourless gas)	Carbonate (CO <sub>3</sub> <sup>2-</sup> )	$\underset{\text{Salt}}{\text{Na}_2\text{CO}_3} + \text{H}_2\text{SO}_4 \longrightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{O} + \text{CO}_2\uparrow$ $\underset{\text{Lime water}}{\text{Ca(OH)}_2} + \text{CO}_2 \longrightarrow \underset{\text{White ppt. (milky)}}{\text{CaCO}_3\downarrow} + \text{H}_2\text{O}$ $\text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2 \longrightarrow \underset{\text{Soluble}}{\text{Ca(HCO}_3)_2}$
H <sub>2</sub> S (Colourless gas with smell of rotten eggs)	Sulphide (S <sup>2-</sup> )	$\underset{\text{Salt}}{\text{Na}_2\text{S}} + \text{H}_2\text{SO}_4 \longrightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{S}\uparrow$ $(\text{CH}_3\text{COO})_2\text{Pb} + \text{H}_2\text{S} \longrightarrow \underset{\text{Black ppt.}}{\text{PbS}\downarrow} + 2\text{CH}_3\text{COOH}$ $\underset{\text{Salt}}{\text{Na}_2\text{S}} + \underset{\text{Sodium nitroprusside}}{\text{Na}_2[\text{Fe(CN)}_5\text{NO}]} \longrightarrow \underset{\text{Violet}}{\text{Na}_4[\text{Fe(CN)}_5\text{NOS}]}$
SO <sub>2</sub> (Colourless gas with suffocating odour having smell of burning sulphur)	Sulphite (SO <sub>3</sub> <sup>2-</sup> )	$\underset{\text{Salt}}{\text{Na}_2\text{SO}_3} + \text{H}_2\text{SO}_4 \longrightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{O} + \text{SO}_2\uparrow$ $\text{K}_2\text{Cr}_2\text{O}_7 + 3\text{SO}_2 + \text{H}_2\text{SO}_4 \longrightarrow \text{K}_2\text{SO}_4 + \underset{\text{Green}}{\text{Cr}_2(\text{SO}_4)_3} + \text{H}_2\text{O}$ $\underset{\text{Salt}}{\text{Na}_2\text{SO}_3} + \text{BaCl}_2 \longrightarrow \underset{\text{White ppt.}}{\text{BaSO}_3\downarrow} + 2\text{NaCl}$ $\text{BaSO}_3 + 2\text{HCl} \longrightarrow \underset{\text{Soluble}}{\text{BaCl}_2} + \text{H}_2\text{O} + \text{SO}_2\uparrow$
NO <sub>2</sub> (Brown gas)	Nitrite (NO <sub>2</sub> <sup>-</sup> )	$\underset{\text{Salt}}{2\text{NaNO}_2} + \text{H}_2\text{SO}_4 \longrightarrow \text{Na}_2\text{SO}_4 + \underset{\text{Nitrous acid}}{2\text{HNO}_2}$ $3\text{HNO}_2 \longrightarrow \text{H}_2\text{O} + 2\text{NO} + \text{HNO}_3$ $2\text{NO} + \text{O}_2 \longrightarrow \underset{\text{Brown}}{2\text{NO}_2\uparrow}$ $\text{FeSO}_4 \cdot 7\text{H}_2\text{O} + \text{NO} \longrightarrow \underset{\text{Brown}}{[\text{Fe(H}_2\text{O)}_5\text{NO}]\text{SO}_4} + 2\text{H}_2\text{O}$
CH <sub>3</sub> COOH (Colourless gas with smell of vinegar)	Acetate (CH <sub>3</sub> COO <sup>-</sup> )	$\underset{\text{Salt}}{2\text{CH}_3\text{COONa}} + \text{H}_2\text{SO}_4 \longrightarrow 2\text{CH}_3\text{COOH} + \text{Na}_2\text{SO}_4$ $\underset{\text{Salt}}{3\text{CH}_3\text{COONa}} + \text{FeCl}_3 \longrightarrow \underset{\text{Blood red}}{(\text{CH}_3\text{COO})_3\text{Fe}} + 3\text{NaCl}$ $\underset{\text{Salt}}{2\text{CH}_3\text{COONa}} + \begin{array}{c} \text{COOH} \\   \\ \text{COOH} \end{array} \longrightarrow \begin{array}{c} \text{COONa} \\   \\ \text{COONa} \end{array} + \underset{\text{Smell of vinegar}}{2\text{CH}_3\text{COOH}}$

Carbonates of Bi and Ba are not easily decomposed by dil. H<sub>2</sub>SO<sub>4</sub> hence, dil. HCl should be used.

- **Second group of acid radicals :** The acid radicals present in this group are chloride (Cl<sup>-</sup>), bromide (Br<sup>-</sup>), iodide (I<sup>-</sup>) and nitrate (NO<sub>3</sub><sup>-</sup>). The group reagent is concentrated sulphuric acid (H<sub>2</sub>SO<sub>4</sub>).

Experiment	Observation	Inference
Salt + conc. H <sub>2</sub> SO <sub>4</sub> and heat (if necessary)	Effervescence or colourless or coloured gases	2 <sup>nd</sup> group of acid radicals is present
	(a) Colourless gas with a pungent smell and gives dense white fumes when a glass rod dipped in ammonium hydroxide (NH <sub>4</sub> OH) is exposed.	The acid radical may be Cl <sup>-</sup> .
	(b) Brown gas evolves which intensifies on addition of MnO <sub>2</sub> .	The acid radical may be Br <sup>-</sup> .
	(c) Deep violet gas evolves.	The acid radical may be I <sup>-</sup> .
	(d) Light brown gas evolves which intensifies on addition of copper turnings.	The acid radical may be NO <sub>3</sub> <sup>-</sup> .



Gas	Radical	Observations and Reactions	Confirmatory tests
<p>HCl (Colourless gas with pungent smell)</p> <p>Cl<sub>2</sub> (Yellowish green, suffocating odour)</p>	Chloride (Cl <sup>-</sup> )	<p>NaCl + H<sub>2</sub>SO<sub>4</sub> → NaHSO<sub>4</sub> + HCl↑ Salt</p> <p>NH<sub>4</sub>OH + HCl → NH<sub>4</sub>Cl↑ + H<sub>2</sub>O White dense fumes</p> <p>HCl + AgNO<sub>3</sub> → AgCl↓ + HNO<sub>3</sub> White ppt.</p> <p>AgCl + 2NH<sub>4</sub>OH → [Ag(NH<sub>3</sub>)<sub>2</sub>]Cl + 2H<sub>2</sub>O Soluble</p> <p>2NaCl + MnO<sub>2</sub> + 3H<sub>2</sub>SO<sub>4</sub> → 2NaHSO<sub>4</sub> + MnSO<sub>4</sub> + 2H<sub>2</sub>O + Cl<sub>2</sub>↑ Salt</p>	<p><b>Chromyl chloride test :</b></p> <p>NaCl + H<sub>2</sub>SO<sub>4</sub> (Conc.) → NaHSO<sub>4</sub> + HCl Salt</p> <p>K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> + 2H<sub>2</sub>SO<sub>4</sub> → 2KHSO<sub>4</sub> + 2CrO<sub>3</sub> + H<sub>2</sub>O</p> <p>CrO<sub>3</sub> + 2HCl → CrO<sub>2</sub>Cl<sub>2</sub>↑ + H<sub>2</sub>O Chromyl chloride (Deep red vapours)</p> <p>CrO<sub>2</sub>Cl<sub>2</sub> + 4NaOH → Na<sub>2</sub>CrO<sub>4</sub> + 2NaCl + 2H<sub>2</sub>O Yellow solution</p> <p>Na<sub>2</sub>CrO<sub>4</sub> + (CH<sub>3</sub>COO)<sub>2</sub>Pb → PbCrO<sub>4</sub>↓ + 2CH<sub>3</sub>COONa Yellow ppt.</p>
Br <sub>2</sub> (Brown gas, intensify on addition of MnO <sub>2</sub> )	Bromide (Br <sup>-</sup> )	<p>NaBr + H<sub>2</sub>SO<sub>4</sub> → NaHSO<sub>4</sub> + HBr Salt</p> <p>2HBr + H<sub>2</sub>SO<sub>4</sub> → Br<sub>2</sub>↑ + 2H<sub>2</sub>O + SO<sub>2</sub> Brown</p> <p>AgNO<sub>3</sub> + NaBr → AgBr↓ + NaNO<sub>3</sub> Pale yellow ppt.</p> <p>AgBr + 2NH<sub>4</sub>OH → [Ag(NH<sub>3</sub>)<sub>2</sub>]Br + 2H<sub>2</sub>O Soluble</p> <p>2NaBr + MnO<sub>2</sub> + 3H<sub>2</sub>SO<sub>4</sub> → 2NaHSO<sub>4</sub> + MnSO<sub>4</sub> + 2H<sub>2</sub>O + Br<sub>2</sub>↑</p>	<p><b>Layer test :</b></p> <p>On treating salt with dil. H<sub>2</sub>SO<sub>4</sub>, CHCl<sub>3</sub> or CCl<sub>4</sub> and chlorine water, brown coloured layer is formed.</p> <p>NaBr + Cl<sub>2</sub> water → 2NaCl + Br<sub>2</sub> Salt</p> <p>Br<sub>2</sub> + CHCl<sub>3</sub> → Brown coloured layer or CCl<sub>4</sub></p>
I <sub>2</sub> (Deep violet vapour, intensify on addition of MnO <sub>2</sub> )	Iodide (I <sup>-</sup> )	<p>2KI + 2H<sub>2</sub>SO<sub>4</sub> → 2KHSO<sub>4</sub> + 2HI Salt</p> <p>2HI + H<sub>2</sub>SO<sub>4</sub> → I<sub>2</sub>↑ + SO<sub>2</sub> + 2H<sub>2</sub>O Violet</p> <p>AgNO<sub>3</sub> + KI → AgI↓ + KNO<sub>3</sub> Yellow ppt.</p> <p>AgI + NH<sub>4</sub>OH → Not soluble</p> <p>2KI + MnO<sub>2</sub> + 3H<sub>2</sub>SO<sub>4</sub> → 2KHSO<sub>4</sub> + MnSO<sub>4</sub> + 2H<sub>2</sub>O + I<sub>2</sub>↑ Salt</p>	<p><b>Layer test :</b></p> <p>2K + Cl<sub>2</sub> → 2KCl + I<sub>2</sub> Salt</p> <p>I<sub>2</sub> + Chloroform → Violet coloured layer</p> <p><b>Starch paper test :</b></p> <p>I<sub>2</sub> + Starch → I<sub>2</sub>-starch complex Violet Blue colour vapours</p>
NO <sub>2</sub> (Light brown gas having pungent smell, intensify on adding Cu turning)	Nitrate (NO <sub>3</sub> <sup>-</sup> )	<p>NaNO<sub>3</sub> + H<sub>2</sub>SO<sub>4</sub> → NaHSO<sub>4</sub> + HNO<sub>3</sub> Salt</p> <p>4HNO<sub>3</sub> → 2H<sub>2</sub>O + 4NO<sub>2</sub>↑ + O<sub>2</sub> Light brown fumes</p> <p>Cu + 4HNO<sub>3</sub> → Cu(NO<sub>3</sub>)<sub>2</sub> + 2NO<sub>2</sub>↑ + 2H<sub>2</sub>O</p>	<p><b>Brown ring test :</b></p> <p>NaNO<sub>3</sub> + H<sub>2</sub>SO<sub>4</sub> → NaHSO<sub>4</sub> + HNO<sub>3</sub> Salt</p> <p>6FeSO<sub>4</sub> + 2HNO<sub>3</sub> + 3H<sub>2</sub>SO<sub>4</sub> (conc.) → 3Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> + 4H<sub>2</sub>O + 2NO Ferrous sulphate</p> <p>[Fe(H<sub>2</sub>O)<sub>6</sub>]SO<sub>4</sub>·H<sub>2</sub>O + NO → [Fe(H<sub>2</sub>O)<sub>5</sub>NO]SO<sub>4</sub> + 2H<sub>2</sub>O Brown ring</p>



- **Group III acidic radicals :** These radicals cannot be detected by either dil.  $\text{H}_2\text{SO}_4$  or conc.  $\text{H}_2\text{SO}_4$ . For detection of these acidic radicals we need some specific tests.

Radical	Observations and Reactions
Sulphate ( $\text{SO}_4^{2-}$ )	$\text{Na}_2\text{SO}_4 + \text{BaCl}_2 \longrightarrow \text{BaSO}_4\downarrow + 2\text{NaCl}$ Salt White ppt.
Phosphate ( $\text{PO}_4^{3-}$ )	$\text{Ca}_3(\text{PO}_4)_2 + 6\text{HNO}_3 \xrightarrow{\text{H}^+} 3\text{Ca}(\text{NO}_3)_2 + 2\text{H}_3\text{PO}_4$ Salt $\text{H}_3\text{PO}_4 + 12(\text{NH}_4)_2\text{MoO}_4 + 21\text{HNO}_3 (\text{Conc.}) \longrightarrow (\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3\downarrow + 21\text{NH}_4\text{NO}_3 + 12\text{H}_2\text{O}$ Ammonium molybdate Canary yellow ppt.
Borate ( $\text{BO}_3^{3-}$ )	$2\text{Na}_3\text{BO}_3 + 3\text{H}_2\text{SO}_4 \longrightarrow 3\text{Na}_2\text{SO}_4 + 2\text{H}_3\text{BO}_3$ Salt $\text{H}_3\text{BO}_3 + 3\text{C}_2\text{H}_5\text{OH} \longrightarrow (\text{C}_2\text{H}_5)_3\text{BO}_3\uparrow + 3\text{H}_2\text{O}$ Ethyl borate (burns with green edged flame)
Fluoride ( $\text{F}^-$ )	$2\text{NaF} + \text{H}_2\text{SO}_4 \longrightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{F}_2$ Salt $\text{SiO}_2 + 2\text{H}_2\text{F}_2 \longrightarrow \text{SiF}_4 + 2\text{H}_2\text{O}$ $3\text{SiF}_4 + 4\text{H}_2\text{O} \longrightarrow \text{H}_4\text{SiO}_4 + 2\text{H}_2\text{SiF}_6$ Silicic acid (Gelatinous white)

**(b) Identification of basic radicals**

- **Separation of basic radicals into different groups :**

Basic radicals of	Group reagent	Precipitated as	Explanation
<b>Group I</b> $\text{Ag}^+, \text{Pb}^{2+}, \text{Hg}_2^{2+}$	dil. HCl	$\text{AgCl}, \text{PbCl}_2, \text{Hg}_2\text{Cl}_2$ (All white)	$K_{sp}$ values of their chlorides are low, hence $K_{ip} > K_{sp}$ and they get precipitated.
<b>Group II</b> $\text{Hg}^{2+}, \text{Pb}^{2+}, \text{Bi}^{3+}, \text{Cu}^{2+}, \text{Cd}^{2+}, \text{As}^{3+}, \text{Sb}^{3+}, \text{Sn}^{2+}, \text{Sn}^{4+}$	$\text{H}_2\text{S}$ in presence of dil. HCl	$\text{HgS}, \text{PbS}, \text{Bi}_2\text{S}_3, \text{CuS}$ (Black); $\text{CdS}, \text{As}_2\text{S}_3, \text{SnS}_2$ (Yellow); $\text{Sb}_2\text{S}_3$ (Orange); $\text{SnS}$ (Brown)	HCl (with common $\text{H}^+$ ion) decreases the ionization of $\text{H}_2\text{S}$ which gives low $[\text{S}^{2-}]$ . Hence, only group II sulphides having low $K_{sp}$ values are precipitated.
<b>Group III</b> $\text{Fe}^{3+}, \text{Cr}^{3+}, \text{Al}^{3+}$	$\text{NH}_4\text{OH}$ in presence of $\text{NH}_4\text{Cl}$	$\text{Fe}(\text{OH})_3$ (Reddish brown), $\text{Cr}(\text{OH})_3$ (Green), $\text{Al}(\text{OH})_3$ (White)	$\text{NH}_4\text{Cl}$ (with common $\text{NH}_4^+$ ion) decreases the ionization of $\text{NH}_4\text{OH}$ giving low $[\text{OH}^-]$ . Hence, only group III hydroxides having low $K_{sp}$ values are precipitated.
<b>Group IV</b> $\text{Zn}^{2+}, \text{Mn}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+}$	$\text{H}_2\text{S}$ in presence of $\text{NH}_4\text{OH}$	$\text{ZnS}$ (Greenish white), $\text{MnS}$ (Buff), $\text{CoS}, \text{NiS}$ (Black),	Basic medium increases the ionization of $\text{H}_2\text{S}$ , thus increasing $[\text{S}^{2-}]$ , hence precipitation of group IV sulphides having high $K_{sp}$ values occurs.
<b>Group V</b> $\text{Ba}^{2+}, \text{Sr}^{2+}, \text{Ca}^{2+}$	$(\text{NH}_4)_2\text{CO}_3$ in presence of $\text{NH}_4\text{OH}$	$\text{BaCO}_3, \text{SrCO}_3, \text{CaCO}_3$ (All white)	$K_{sp}$ values of their carbonates are less than that of group VI ( $\text{Mg}^{2+}$ ) hence, group V is precipitated before $\text{Mg}^{2+}$ .
<b>Group VI</b> $\text{Mg}^{2+}$	$\text{Na}_2\text{HPO}_4$ in presence of $\text{NH}_4\text{OH}$	$\text{Mg}(\text{NH}_4)\text{PO}_4$ (White)	—
<b>Zero</b> $\text{NH}_4^+$	$\text{NaOH}$	Ammonia gas is evolved.	Tested independently from original solution.

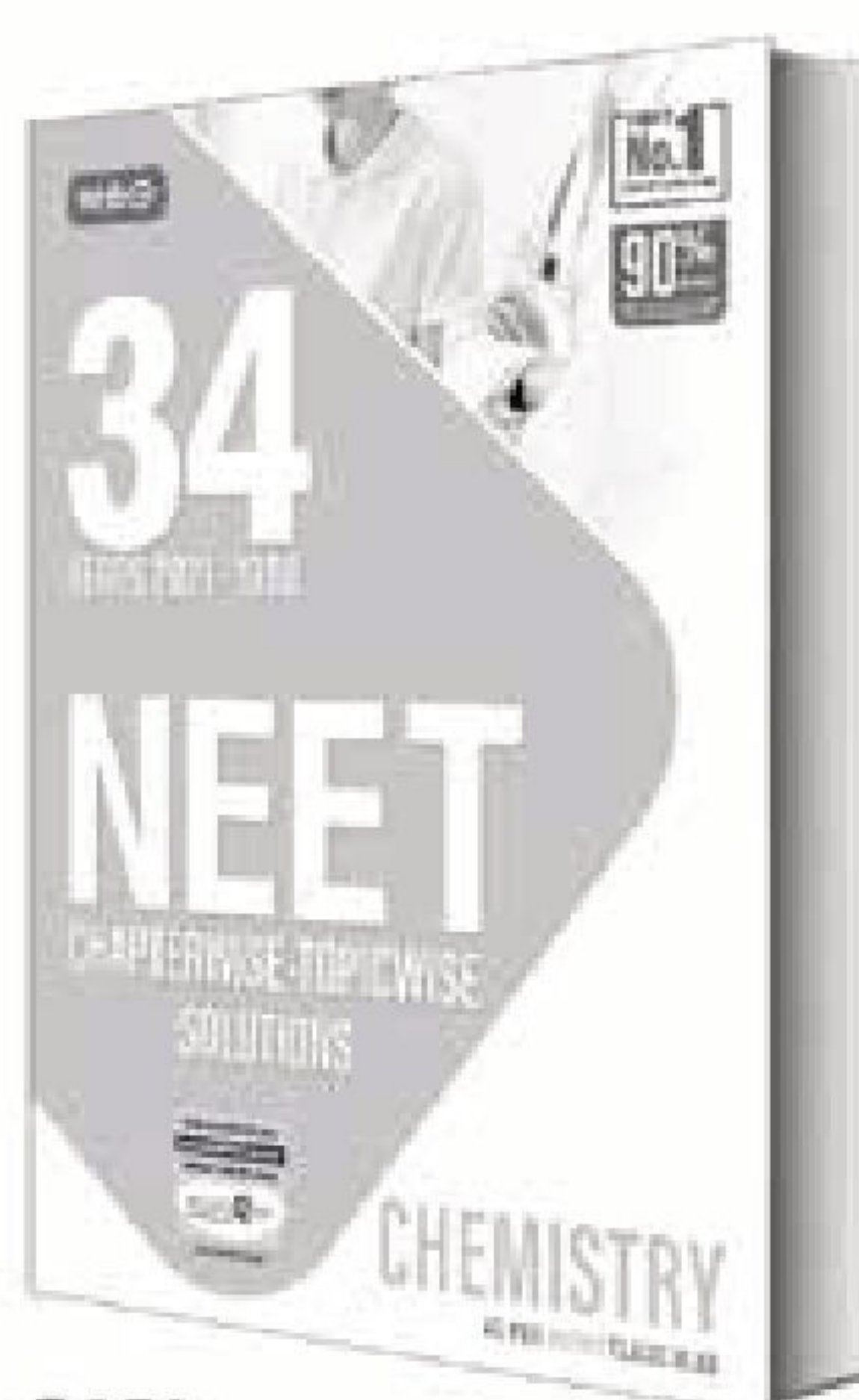


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● **Identification & confirmation of basic radicals :**

- **Preparation of original solution :** A suitable solvent is found for the salt as given in the preliminary test. A few drops of solution are used for the tests.  
Test for  $\text{NH}_4^+$  radicals : This test is carried out before starting the analysis for the basic radicals.

Experiment	Observation	Inference
(a) Salt + NaOH solution and heat it.  Expose a glass rod dipped in conc. HCl to the gas and moist red litmus paper.	Colourless gas with a pungent smell is obtained. Dense white fumes and moist red litmus paper turns blue.	$\text{NH}_4^+$ may be present in the salt.
(b) Pass the gas through Nessler's reagent.	Brown solution or ppt. is obtained.	$\text{NH}_4^+$ is confirmed.

– **First group of basic radicals**

Experiment	Observation	Inference
(1) Original solution + dilute HCl	White ppt. is formed.	May be $\text{Pb}^{2+}$ and $\text{Ag}^+$
Filter and add water to ppt. and heat.	(a) ppt. dissolves in hot water.	May be $\text{Pb}^{2+}$
	(b) ppt. is insoluble in water.	May be $\text{Ag}^+$
(2) Solution (1a) + potassium chromate solution	A yellow ppt. is formed.	$\text{Pb}^{2+}$ is confirmed.
(3) Solution (1a) + KI solution ppt. obtained + water and heat it.	A yellow ppt. soluble in hot water.	$\text{Pb}^{2+}$ is confirmed.

– **Second group of basic radicals**

Experiment	Observation	Inference
Original solution + dilute HCl + $\text{H}_2\text{S}$ gas. or (Group I filtrate)	(a) Black ppt.	May be $\text{Pb}^{2+}$ , $\text{Hg}^{2+}$ and $\text{Cu}^{2+}$
	(b) A yellow ppt.	May be $\text{Cd}^{2+}$

- The identification of  $\text{Pb}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  are as follows :

Experiment	Observation	Inference
(a) Original solution + potassium chromate	A yellow ppt. is observed.	$\text{Pb}^{2+}$ is confirmed.
(b) Original solution + $\text{NH}_4\text{OH}$	A bluish white ppt. soluble in excess of $\text{NH}_4\text{OH}$ forming a blue solution.	May be $\text{Cu}^{2+}$
(c) Add dil. acetic acid + potassium ferrocyanide solution to the blue solution	A chocolate brown ppt. is obtained.	$\text{Cu}^{2+}$ is confirmed
(d) Dissolve the black ppt. in aqua regia + 1 mL of distilled water, heat and add 2 drops of $\text{SnCl}_2$	A white ppt. is observed which turns grey.	$\text{Hg}^{2+}$ is confirmed.
(e) Original solution + dilute acetic acid + $\text{H}_2\text{S}$ gas	A yellow ppt. is formed.	$\text{Cd}^{2+}$ is confirmed.



● **Third group of basic radicals**

Experiment	Observation	Inference
(1) Group II filtrate + $\text{NH}_4\text{Cl}_{(s)}$ + $\text{NH}_4\text{OH}$ in excess. ( $\text{H}_2\text{S}$ boiled off)	(a) A white gelatinous ppt. is obtained.	May be $\text{Al}^{3+}$
	(b) A dirty green ppt. is obtained.	May be $\text{Fe}^{2+}$
	(c) A reddish brown ppt. is obtained.	May be $\text{Fe}^{3+}$
(2) Precipitate (a, b or c) + $\text{NaOH}$ solution.	(a) White gelatinous ppt. soluble in excess of $\text{NaOH}$ gives a colourless solution.	The basic radical is $\text{Al}^{3+}$ .
	(b) Dirty green ppt. insoluble in excess of $\text{NaOH}$ .	The basic radical is $\text{Fe}^{2+}$ .
	(c) Reddish brown ppt. insoluble in excess of $\text{NaOH}$ .	The basic radical is $\text{Fe}^{3+}$ .
(3) Clear solution of 2(a) + solid $\text{NH}_4\text{Cl}$ and heat.	The white gelatinous ppt. reappears.	$\text{Al}^{3+}$ is confirmed.
(4) Dissolve 2(c) ppt. in dil. $\text{HCl}$ and divide in two parts : Part I + $\text{K}_4[\text{Fe}(\text{CN})_6]$ Part II + $\text{KCNS}$	(a) Prussian blue colour.	$\text{Fe}^{3+}$ is confirmed.
	(b) Blood red colour	

● **Fourth group of basic radicals**

Experiment	Observation	Inference
(1) Group III filtrate + $\text{NH}_4\text{Cl}_{(s)}$ + $\text{NH}_4\text{OH}$ and excess of $\text{H}_2\text{S}_{(g)}$	(a) A white ppt. is obtained.	May be $\text{Zn}^{2+}$
	(b) Buff or pale pink or flesh coloured ppt. soluble in dilute $\text{HCl}$ is obtained.	May be $\text{Mn}^{2+}$
	(c) Black ppt. is obtained.	May be $\text{Co}^{2+}$ or $\text{Ni}^{2+}$
(2) Precipitate + $\text{NaOH}$ solution	(a) The white ppt. is soluble in excess of $\text{NaOH}$ giving a colourless solution.	$\text{Zn}^{2+}$ is confirmed.
	(b) The white ppt. insoluble in excess of $\text{NaOH}$ but turns brown on addition of $\text{Br}_2$ .	$\text{Mn}^{2+}$ is confirmed.
(3) Dissolve 1(a) in aqua regia, evaporate to dryness, add 1 mL of distilled water and divide the resultant product into two parts : Part (1) + 1 mL of ether + 100 mg of solid $\text{NH}_4\text{SCN}$ and stir it. Part (2) + 5 drops of dimethyl glyoxime reagent + $\text{NH}_4\text{OH}$ .	A blue colour in the alcohol layer is obtained.	$\text{Co}^{2+}$ is confirmed
	A pink ppt. is obtained.	$\text{Ni}^{2+}$ is confirmed



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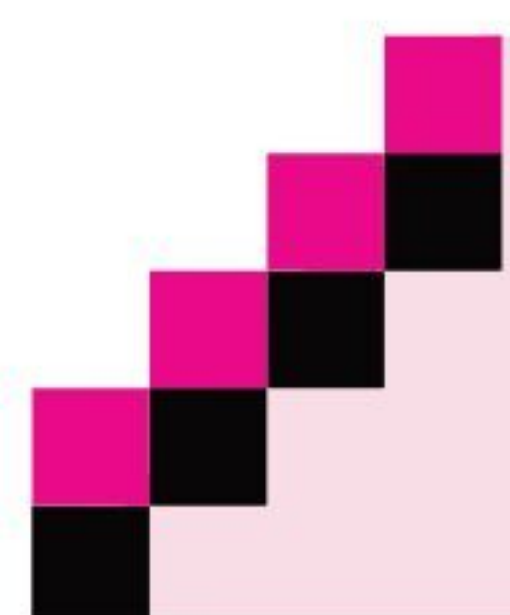


● **Fifth group of basic radicals**

Experiment	Observation	Inference
(1) Group IV filtrate ( $\text{H}_2\text{S}$ boiled off) + $\text{NH}_4\text{Cl}_{(s)}$ + $\text{NH}_4\text{OH}$ in excess + $(\text{NH}_4)_2\text{CO}_3$ solution.	A white ppt. is obtained	May be $\text{Ca}^{2+}$ , $\text{Sr}^{2+}$ or $\text{Ba}^{2+}$
(2) Dissolve the white ppt. obtained in small amounts of dilute acetic acid. Divide the solution in three parts : Part (1) + potassium chromate solution. Part (2) + ammonium sulphate solution and heat. Part (3) + ammonium oxalate solution.	(a) A yellow ppt. is obtained	May be $\text{Ba}^{2+}$
	(b) A white ppt. is obtained	May be $\text{Sr}^{2+}$
	(c) A white ppt. is obtained	May be $\text{Ca}^{2+}$
(3) <b>Flame tests</b> : Make a paste of the given salt with few drops of conc. $\text{HCl}$ in a watch glass. Heat a Pt wire in non-luminous flame till no colour is imparted to the flame. Dip the Pt wire in the paste and hold it in the flame.	(a) Apple green coloured flame	$\text{Ba}^{2+}$ is confirmed
	(b) Crimson red coloured flame	$\text{Sr}^{2+}$ is confirmed
	(c) Brick red coloured flame	$\text{Ca}^{2+}$ is confirmed

● **Sixth group of basic radicals**

Experiment	Observation	Inference
(1) Group V filtrate + excess of $\text{NH}_4\text{OH}$ + ammonium hydrogen phosphate.	A white ppt. is obtained.	$\text{Mg}^{2+}$ is confirmed



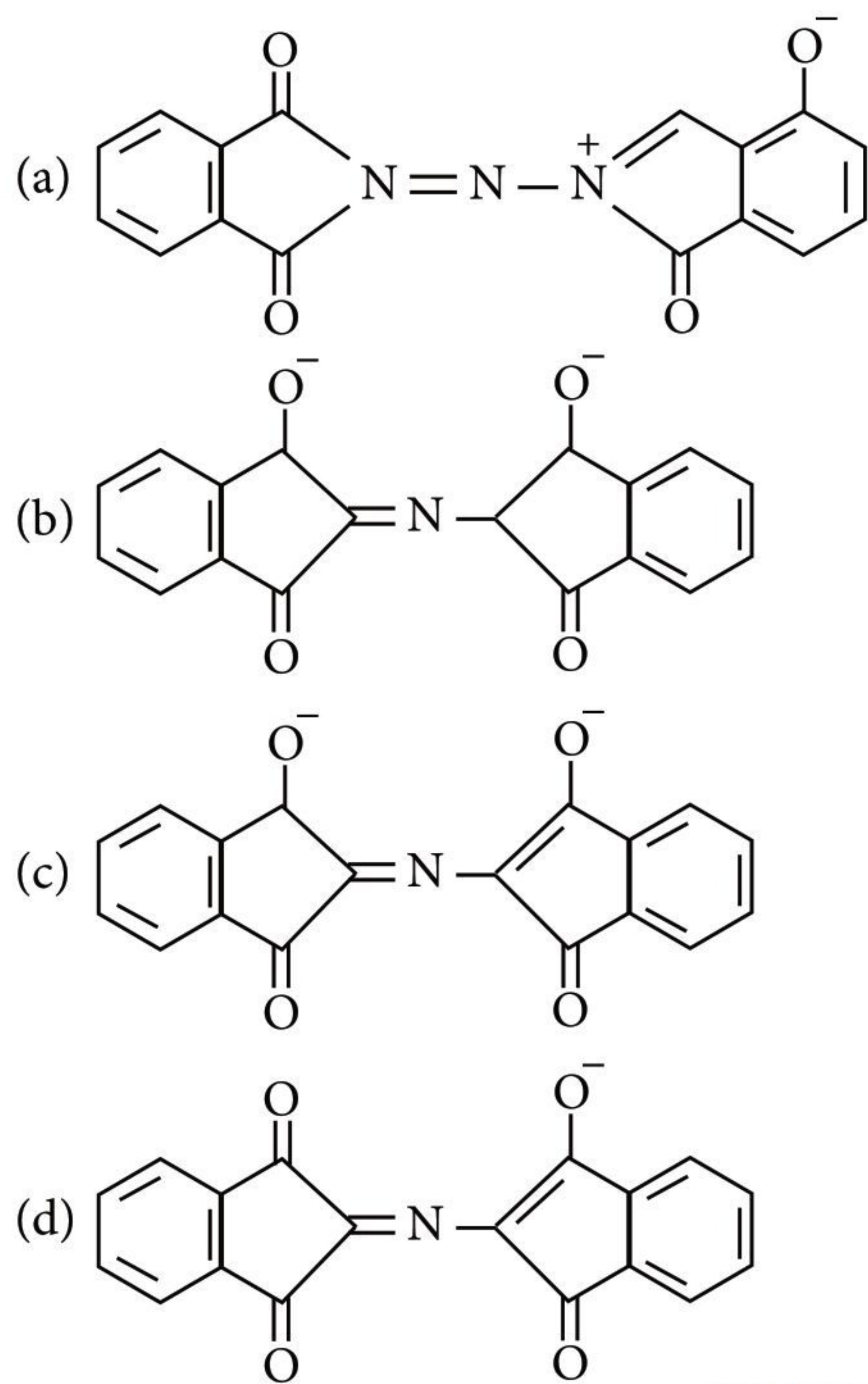
# WRAP it up!

## MCQs Type

- Aldehydes and ketones can be distinguished from each other by
  - ferric chloride test
  - silver mirror test
  - litmus test
  - DNP test.
- A salt on reacting with dil.  $\text{H}_2\text{SO}_4$  gives a reddish brown gas. The salt is
  - $\text{KNO}_2$
  - $\text{ZnBr}_2$
  - $\text{NaNO}_3$
  - none of these.
- There are several criteria of purity of organic compounds. Which is considered to be the best?
  - Melting point
  - Mixed melting point
  - Colour
  - Microscopic examination
- Acetanilide finds application in medicine as
  - hypnotic
  - antiseptic
  - antipyretic
  - antimalarial.
- Statement-1** : Sodium extract is made alkaline in the test of sulphur.  
**Statement-2** : On reacting with  $\text{FeCl}_3$ , alkaline sodium extract, gives red colour.
  - Both statement-1 and statement-2 is true and statement - 2 is a correct explanation for statement-1.
  - Both statement-1 and statement-2 is true but statement-2 is not a correct explanation for statement-1.
  - Statement-1 is true but Statement-2 is false.
  - Statement-1 is false but Statement-2 is true.
- In the study of oxidation of  $\text{I}^-$  ions by  $\text{H}_2\text{O}_2$  in presence of dilute  $\text{H}_2\text{SO}_4$ , thiosulphate and starch as a clock reaction, if concentration of iodide ions is decreased then
  - more time will be taken for blue colour to appear
  - less time will be taken for blue colour to appear
  - same time will be taken for blue colour to appear
  - blue colour will not appear at all.



7. The correct structure of Rhumann's Purple, the compound formed in the reaction of ninhydrin with proteins is



(JEE Main 2021)

8. The essential condition for an indicator to be used in a titration is
- $pK_{In} = pK_a$  of solution at equivalence point
  - $pK_{In} = pK_b$  of solution at equivalence point
  - $pK_{In} = pH$  of solution at equivalence point
  - $pK_{In} = pK_a + pK_b$  of solution at equivalence point.
9. Aniline on heating with conc.  $HNO_3$  + conc.  $H_2SO_4$  mixture yields
- o*- and *p*-nitroanilines
  - m*-nitroaniline
  - a black tarry matter
  - no reaction.
10. When  $H_2S$  is passed through an ammoniacal salt solution X, a white precipitate is obtained. X can be a
- cobalt salt
  - nickel salt
  - manganese salt
  - zinc salt.
11. Generally it is more difficult to purify organic compounds than inorganic compounds because
- they are very unstable
  - their melting point and boiling point are low
  - organic compounds have low solubility
  - physical constants of organic compounds and the impurities associated with them are very close to each other.
12. In the qualitative analysis of third group, the reagent mixture of  $NH_4Cl$  and  $NH_4OH$  is employed. If  $NH_4Cl$  is not available and the mixture does not contain  $Mn^{2+}$ , which of the following can be used?
- $(NH_4)_2SO_4$
  - $(NH_4)_2CO_3$
  - $NH_4NO_3$
  - All of these
13. Why are strong acids generally used as standard solution in acid-base titration?
- The pH at equivalence point is always 7.
  - They can be used to titrate both strong and weak bases.
  - Strong acids form more stable solutions than weak acids.
  - The salts of strong acid do not hydrolyse.
14. Which of the following statements is correct?
- $Fe^{2+}$  gives brown colour with ammonium thiocyanate.
  - $Fe^{2+}$  gives blue precipitate with potassium ferricyanide.
  - $Fe^{3+}$  gives green colour with potassium ferricyanide.
  - $Fe^{3+}$  gives red colour with potassium ferrocyanide.
15. For which of the following compounds Lassaigne's test of nitrogen will fail?
- $H_2NCONHNH_2 \cdot HCl$
  - $H_2NNH_2 \cdot 2HCl$
  - $H_2NCONH_2$
  - $C_6H_5 - N = N - C_6H_5$
16. The strength of an aqueous NaOH solution is most accurately determined by titrating (Note : consider that an appropriate indicator is used.)
- aq. NaOH in a pipette and aqueous oxalic acid in a burette
  - aq. NaOH in a volumetric flask and concentrated  $H_2SO_4$  in a conical flask
  - aq. NaOH in a burette and concentrated  $H_2SO_4$  in a conical flask
  - aq. NaOH in a burette and aqueous oxalic acid in a conical flask.
17. pH indicators are
- salts of strong acids and strong bases
  - salts of weak acids and weak bases
  - either weak acids or weak bases
  - either strong acids or strong bases.



18. An alkali is titrated against an acid with methyl orange as indicator, which of the following is a correct combination?

Base	Acid	End point
(a) Weak	Strong	Colourless to pink
(b) Strong	Strong	Pinkish red to yellow
(c) Weak	Strong	Yellow to pinkish red
(d) Strong	Strong	Pink to colourless

(JEE Main 2018)

19. Sodium nitroprusside when added to an alkaline solution of sulphide ions produce a
- (a) red colouration (b) blue colouration  
(c) purple colouration (d) brown colouration.

20. If NaOH is added to an aqueous solution of zinc ions a white precipitate appears and on adding excess NaOH, the precipitate dissolves. In this solution zinc exists in the
- (a) cationic part  
(b) anionic part  
(c) both in cationic and anionic parts  
(d) there is no zinc ion in the solution.

21. Which of the following is not suitable in  $\text{KMnO}_4$  titrations?
- (a) Burette with glass stopper  
(b) Burette with rubber pinch cock  
(c) Glass pipette  
(d) Glass titration flask

22. Given below are two statements:

**Statement-I:** In the titration between strong acid and weak base methyl orange is suitable as an indicator.

**Statement-II:** For titration of acetic acid with NaOH phenolphthalein is not a suitable indicator.

- (a) Statement-I is false but statement-II is true.  
(b) Both statement-I and statement-II are true.  
(c) Both statement-I and statement-II are false.  
(d) Statement-I is true but statement-II is false.

(JEE Main 2021)

23. Which of the following is not done on boiling the sodium extract with conc.  $\text{HNO}_3$  during test of halogens by silver nitrate?
- (a) Decomposition of sodium halide if present  
(b) Decomposition of sodium cyanide if present  
(c) Decomposition of sodium sulphide if present  
(d) Acidification of sodium extract.

24. Oxalic acid dihydrate,  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}_{(s)}$  is often used as a primary reagent to standardise sodium

hydroxide solution. Which of these facts are reasons to choose this substance as a primary standard?

- I. It is diprotic.  
II. It is a stable compound that can be weighed directly in air.  
III. It is available in pure form.
- (a) III only (b) I and II only  
(c) II and III only (d) I, II and III

25. In organic compounds, halogens are estimated by
- (a) Liebig method  
(b) Carius method  
(c) Schiff's and Piria method  
(d) both (b) and (c).

### NUMERICAL VALUE TYPE

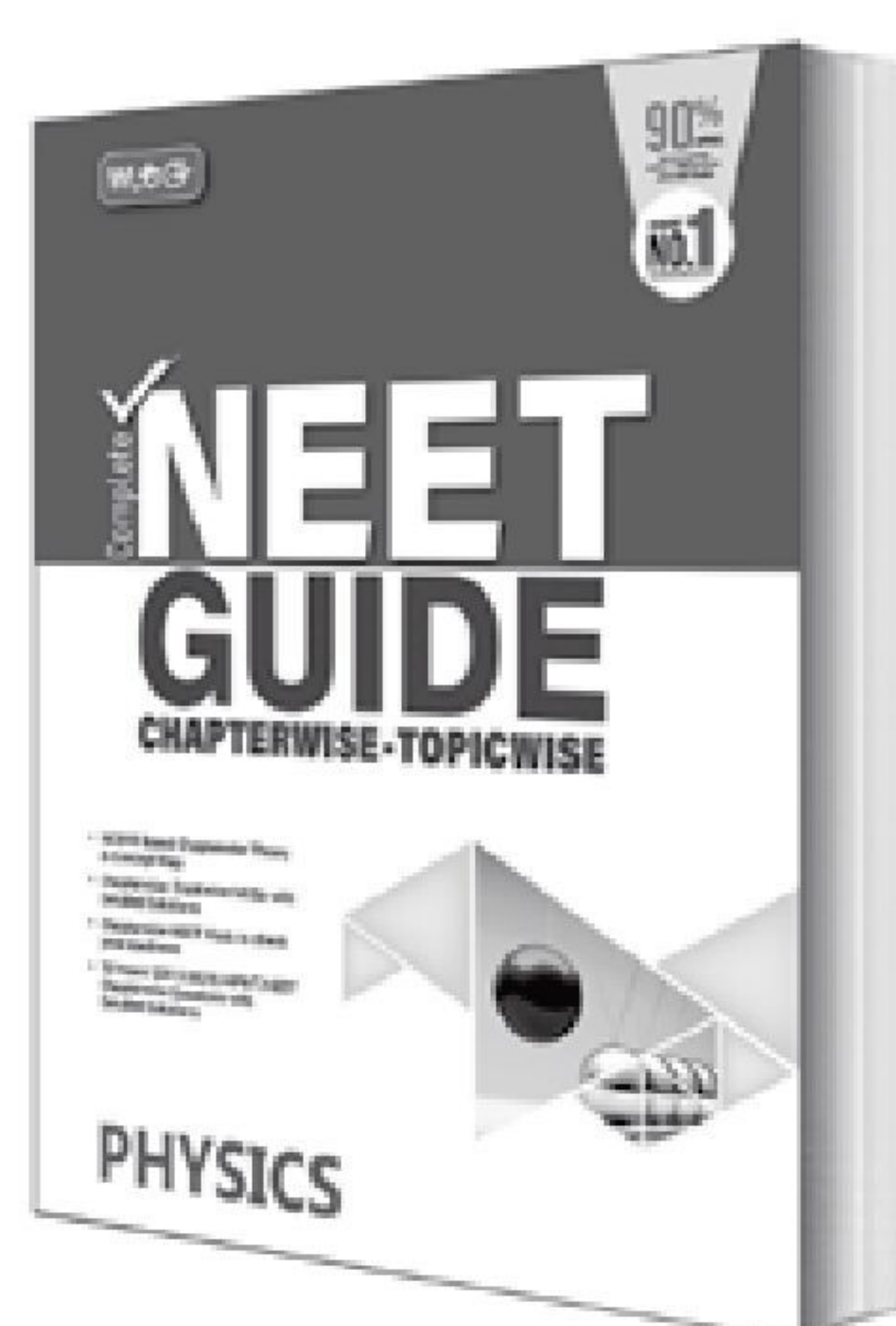
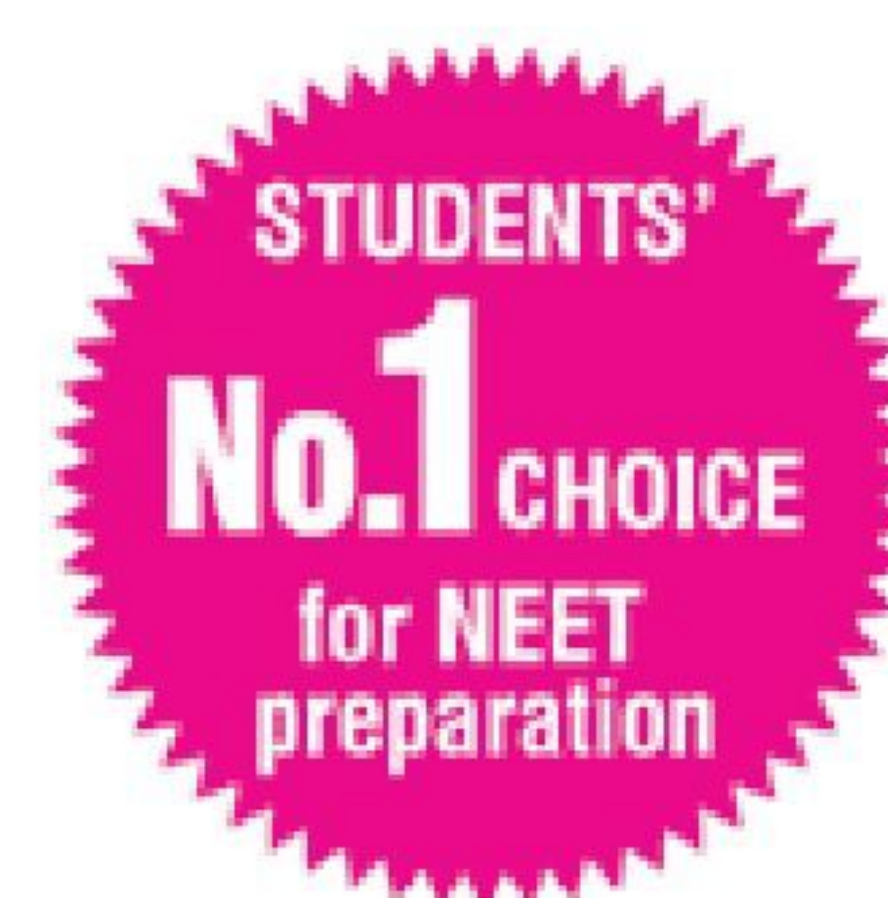
26. 1 mole of  $\text{KMnO}_4$  reacts with  $x$  moles of oxalic acid. Value of  $x$  is \_\_\_\_\_.
27. Sulphur present in organic compound is  $xy\%$ , if 0.53 g compound has 1.158 g  $\text{BaSO}_4$ . The value of  $(x + y)$  is \_\_\_\_\_.
28. 0.126 g of acid requires 20 mL of 0.1 N NaOH for complete neutralization. The equivalent mass of the acid is \_\_\_\_\_.
29. Consider the sulphides  $\text{HgS}$ ,  $\text{PbS}$ ,  $\text{CuS}$ ,  $\text{Sb}_2\text{S}_3$ ,  $\text{As}_2\text{S}_3$  and  $\text{CdS}$ . Number of these sulphides soluble in 50%  $\text{HNO}_3$  is \_\_\_\_\_. (JEE Main 2021)
30. 0.28 g of an organic compound was heated with conc.  $\text{H}_2\text{SO}_4$  and then distilled with NaOH to produce  $\text{NH}_3$ .  $\text{NH}_3$  gas is passed through 50 mL  $\text{N}/10$   $\text{H}_2\text{SO}_4$ . Remaining acid required 40 mL  $\text{N}/10$  alkali for complete neutralization. Calculate percentage of nitrogen in the compound.

### SOLUTIONS

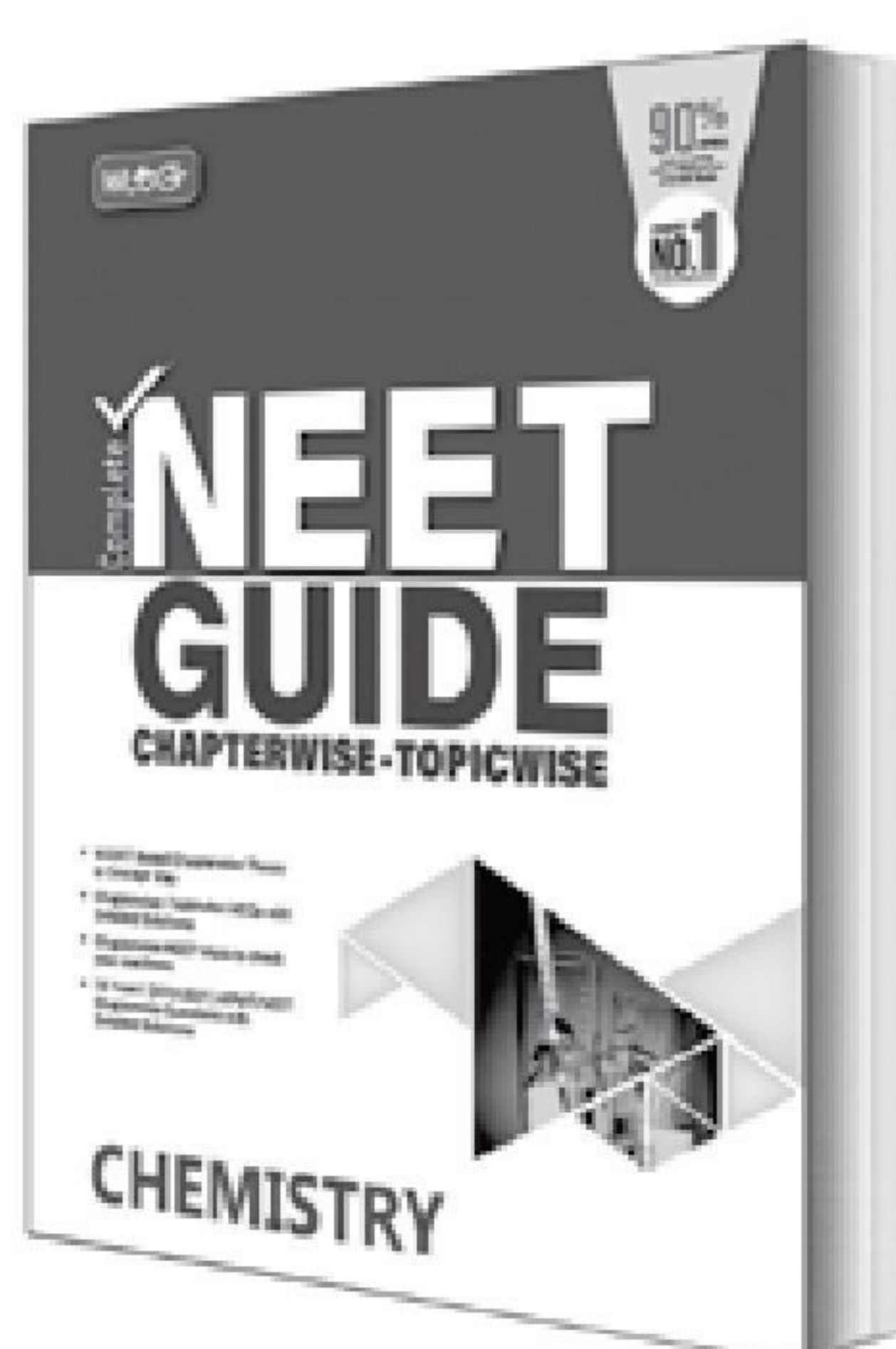
1. (b) : Aldehydes and ketones can be distinguished by silver mirror test. Aldehydes give positive test.
2. (a) :  $2\text{KNO}_2 + \text{H}_2\text{SO}_4 \longrightarrow \text{K}_2\text{SO}_4 + 2\text{HNO}_2$   
 $3\text{HNO}_2 \longrightarrow \text{HNO}_3 + \text{H}_2\text{O} + 2\text{NO}$   
 $2\text{NO} + \text{O}_2 (\text{air}) \longrightarrow 2\text{NO}_2 \uparrow$   
 reddish brown
3. (b) : Mixed melting point is considered to be the best criteria for purity of a substance. The purified sample is mixed with a small quantity of pure compound and melting point of mixture is determined. If melting point of mixture is same as that of the pure compound, the sample compound is pure, otherwise it requires further purification.
4. (c) : Acetanilide has antipyretic application.



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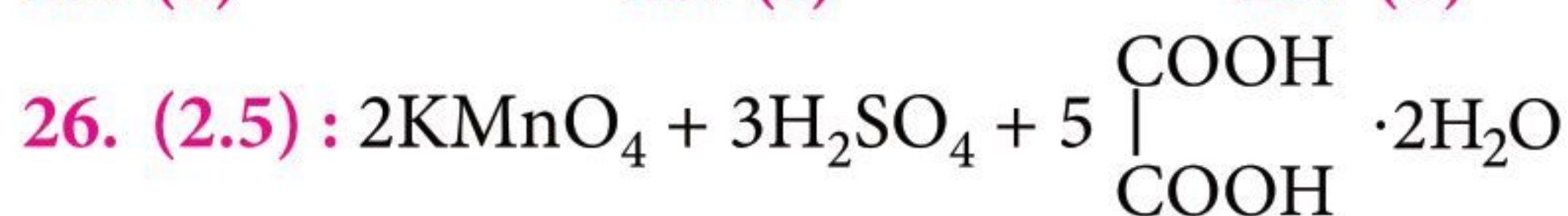
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5. (d) : In the Lassaigne's test for sulphur, sodium extract is made acidic before the addition of lead acetate, because the black precipitate of lead sulphide is insoluble in acidic medium.
6. (a) : If concentration of iodide ions is decreased, the reaction will be slow and hence will take more time to react with thiosulphate added and for blue colour to appear.
7. (d)
8. (c) : For an indicator to be used,  $pK_{In} = pH$  of solution at equivalence point.
9. (c) : Aniline cannot undergo direct nitration. Since  $HNO_3$  is a strong oxidising agent, it oxidises aniline to a black tarry mass.
10. (d) : Zinc salt solution on passing  $H_2S$  in presence of  $NH_4OH$  gives a white or dirty white ppt. of  $ZnS$ .
11. (d) : In organic compounds, impurities also have very close physical constants/properties.
12. (c)
13. (b) : Strong acid can be used to titrate both strong and weak bases.
14. (b) :  $Fe^{2+}$  gives blue ppt. with potassium ferricyanide of prussian blue complex.
15. (b) :  $H_2NNH_2 \cdot 2HCl$  does not contain carbon, hence does not give positive results for Lassaigne's test for nitrogen.
16. (d)
17. (c) : pH indicators are generally complex organic molecules which are either weak acids (e.g., phenolphthalein) or weak bases (e.g., methyl orange).
18. (c) : Methyl orange shows yellow colour in basic medium and red colour in acidic medium.
19. (c) : Sodium nitroprusside + sulphide ions  $\xrightarrow{\text{Alkali}}$  purple colour.
20. (b) :  $Zn^{2+} + 2NaOH \longrightarrow Zn(OH)_2 + 2Na^+$   
(White ppt.)  
 $Zn(OH)_2 + 2NaOH \longrightarrow Na_2ZnO_2 + 2H_2O$   
(soluble)
21. (b)
22. (d) : Methyl orange is a good chemical indicator in strong acid and weak base titration as it changes its yellow colour in basic to red colour in acidic medium. Phenolphthalein is used as indicator for weak acid and strong base titration as it changes colour between pH range 8 to 10.

23. (a)                      24. (c)                      25. (d)



It is obvious from the equation that two moles of  $KMnO_4$  react with five moles of oxalic acid. Thus, one mole of  $KMnO_4$  will react with 2.5 moles of oxalic acid.

27. (3) : % of S =  $\frac{32}{233} \times \frac{W_1}{W} \times 100$

where  $W_1$  = mass of  $BaSO_4$

and  $W$  = mass of organic compound

$\Rightarrow$  % of S =  $\frac{32}{233} \times \frac{1.158}{0.53} \times 100 = 30\% \Rightarrow x + y = 3$


28. (63) : Milliequivalent of acid = Milliequivalent of NaOH

$\frac{0.126}{\text{Equivalent weight}} \times 1000 = 0.1 \times 20$

Equivalent weight = 63

29. (4) :  $CdS$ ,  $PbS$ ,  $As_2S_3$  and  $CuS$  are soluble in 50%  $HNO_3$ .


30. (5) : Percentage of nitrogen =  $\frac{1.4}{W} (N_1V_1 - N_2V_2)$   
 $= \frac{1.4}{0.28} \left( 50 \times \frac{1}{10} - 40 \times \frac{1}{10} \right) = \frac{1.4}{0.28} (5 - 4) = \frac{1.4 \times 1}{0.28} = 5$



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# LEARNFAST

## ESSENTIALS FOR TERM-II

Aldehydes, Ketones and Carboxylic Acids | Amines

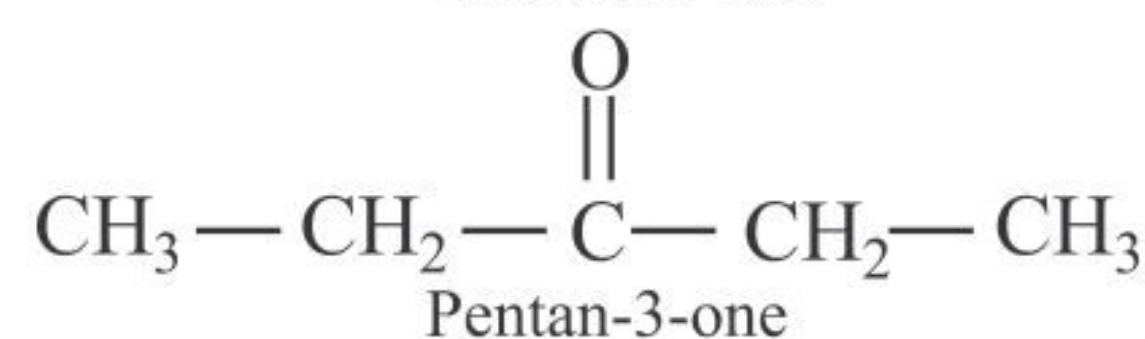
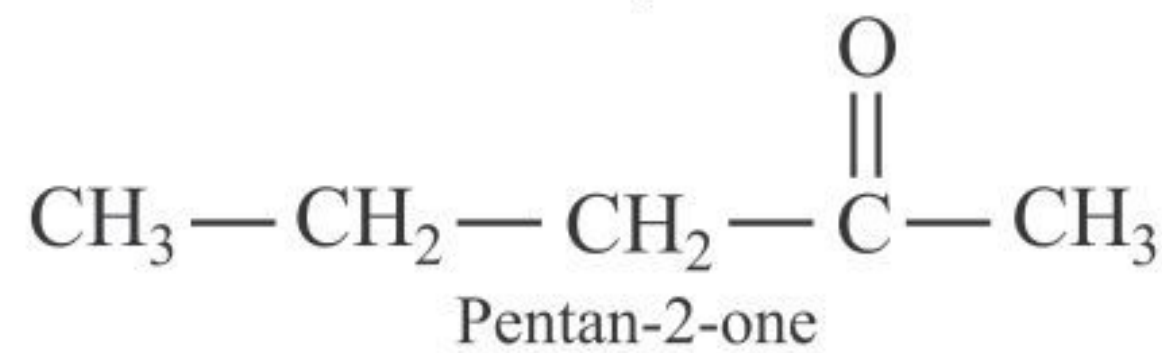
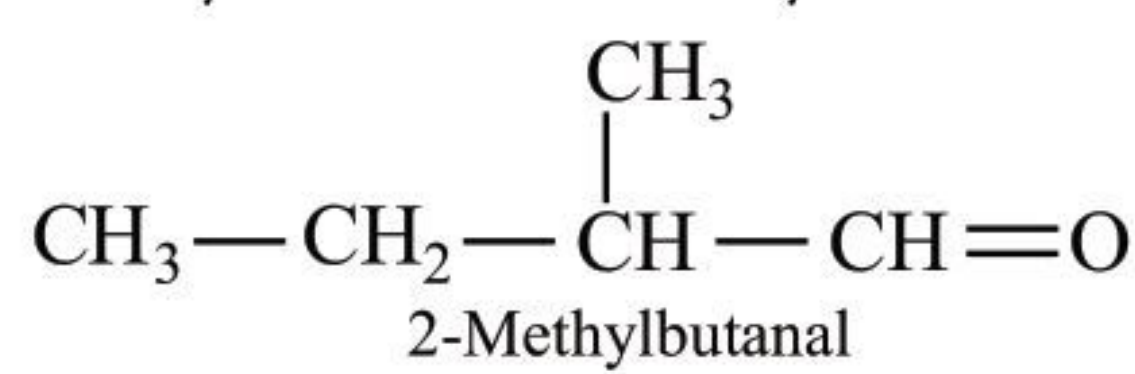
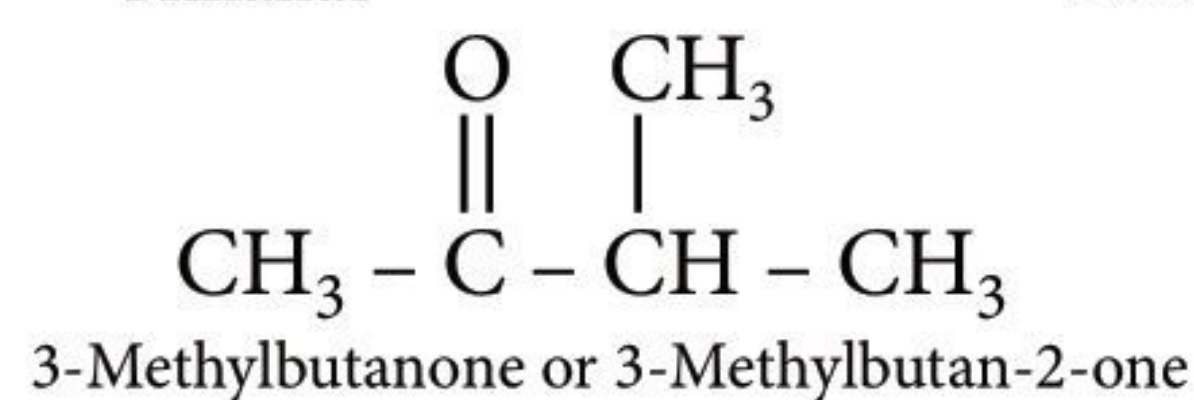
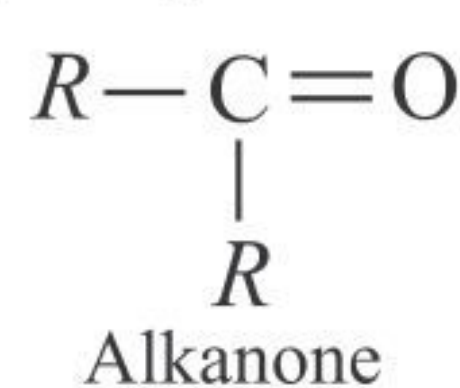
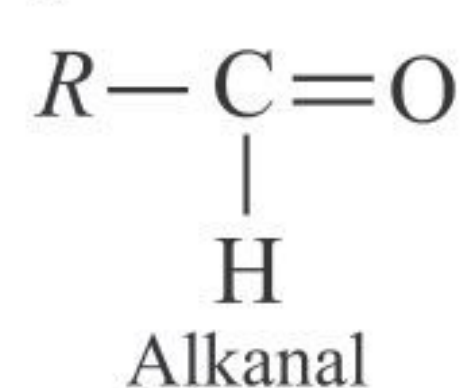


### ALDEHYDES AND KETONES

Compounds containing  $\text{>C=O}$  (carbonyl) group are collectively known as **carbonyl compounds**. If one of the valencies of carbonyl carbon is satisfied by H-atom, then the compounds are known as **aldehydes** and have general formula  $R\text{CHO}$  (where  $R$  may be H or alkyl group). If both the valencies are satisfied by alkyl group, then the compound is said to be **ketone** ( $R\text{COR}$ ). Both aldehydes and ketones have general formula,  $\text{C}_n\text{H}_{2n}\text{O}$ .

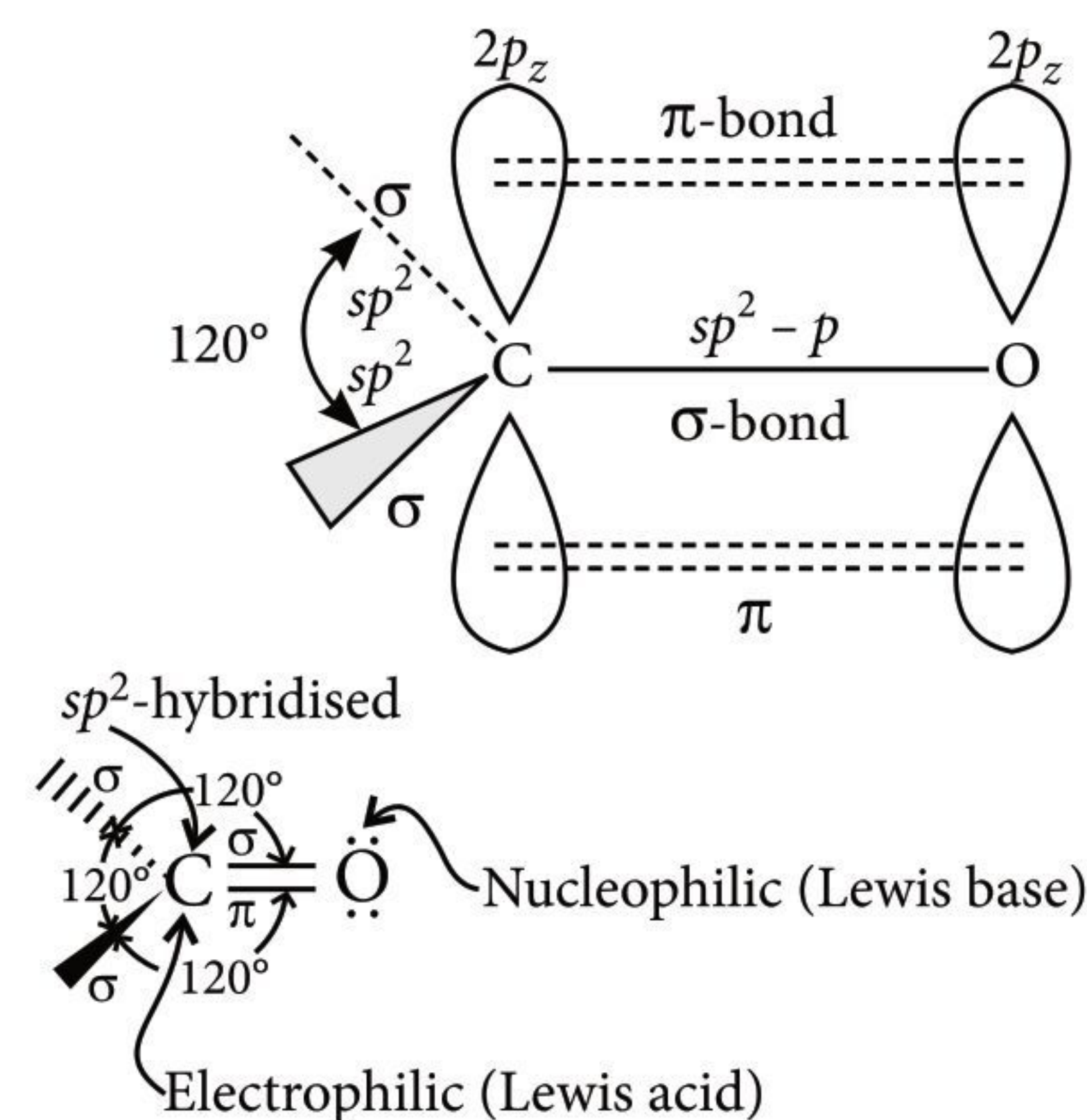
#### Nomenclature

- ◆ According to IUPAC name 'e' of alkane is replaced by 'al' in case of aldehyde and 'e' of alkane is replaced by 'one' in case of ketone. Aldehyde is always at terminal hence position of aldehydic group is normally not indicated. In case of ketone we use position of carbonyl group whenever it is needed.

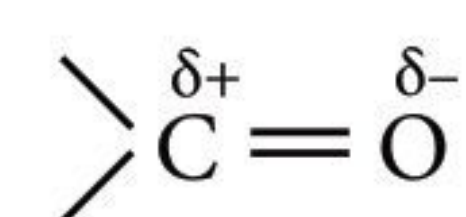


#### Structure and Nature of the Carbonyl Group

- ◆ The  $\text{C}=\text{O}$  bond in aldehydes and ketones like the  $\text{C}=\text{C}$  bond in alkenes is made up of one  $\sigma$ -bond and one  $\pi$ -bond. In the formation of carbonyl group, C uses  $sp^2$ -hybrid orbitals while O uses its unhybridised atomic orbitals.



- ◆ The electrons in the  $\pi$  bond of the carbonyl group are not equally shared i.e., they are pulled towards the more electro-negative oxygen atom. This results in polarization of bond.



### COMIC CAPSULE

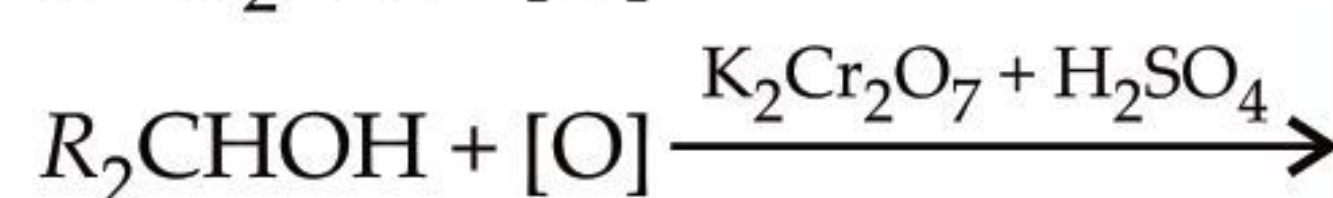
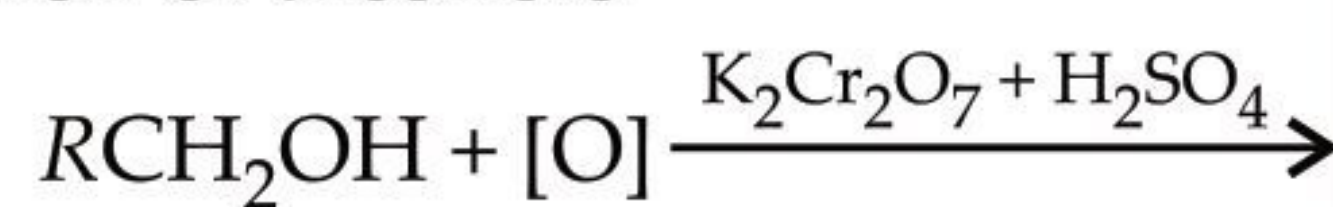


If Iron Man and Silver Surfer teamed up, they'd be alloys.

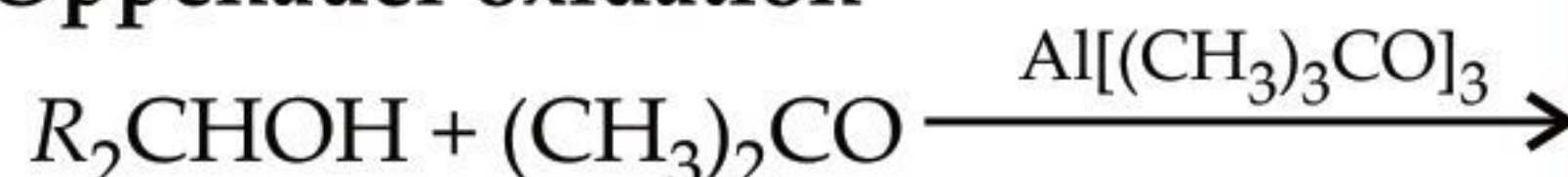


## Methods of Preparation

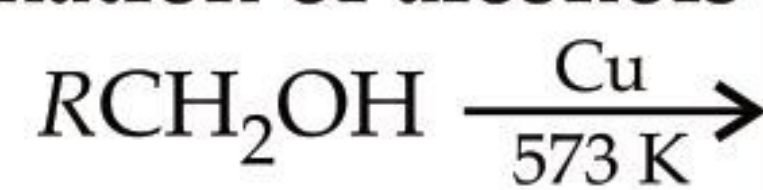
### Oxidation of alcohols



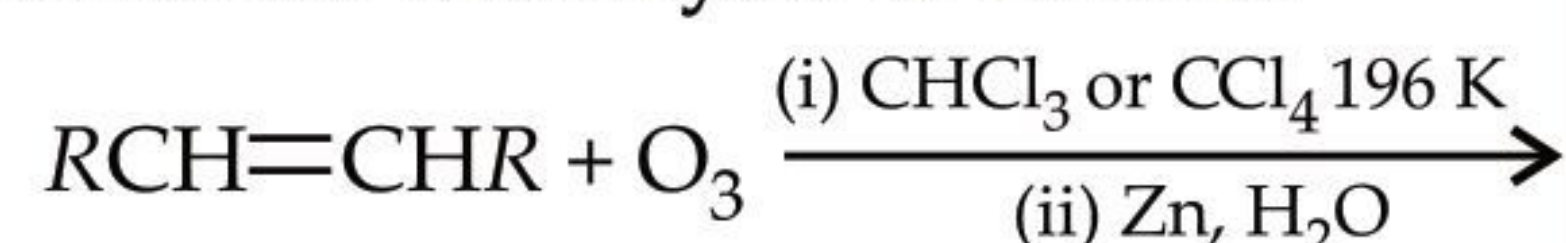
### Oppenauer oxidation



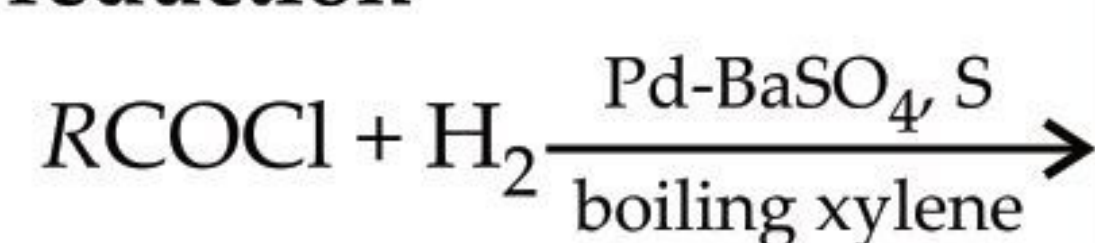
### Catalytic dehydrogenation of alcohols



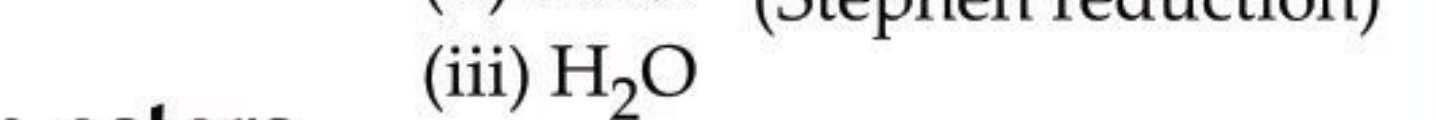
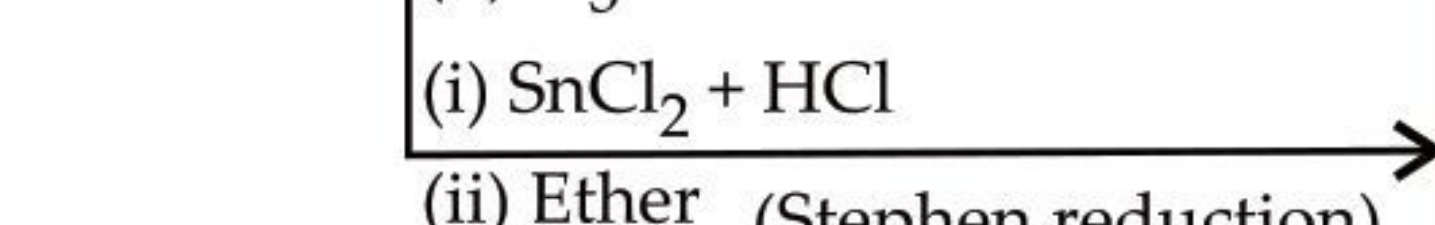
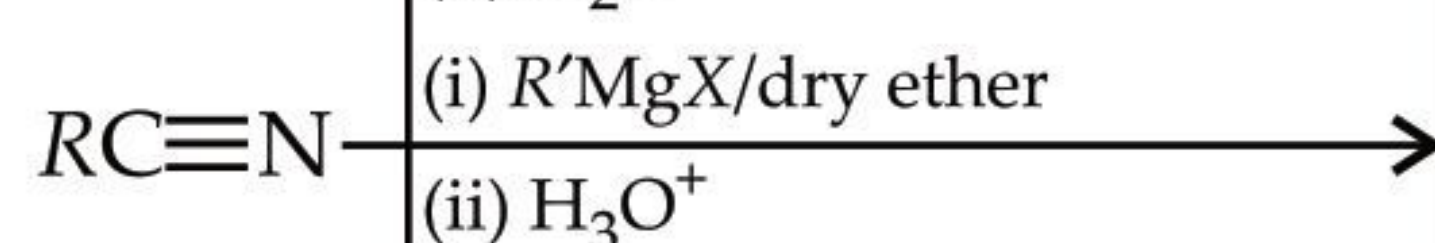
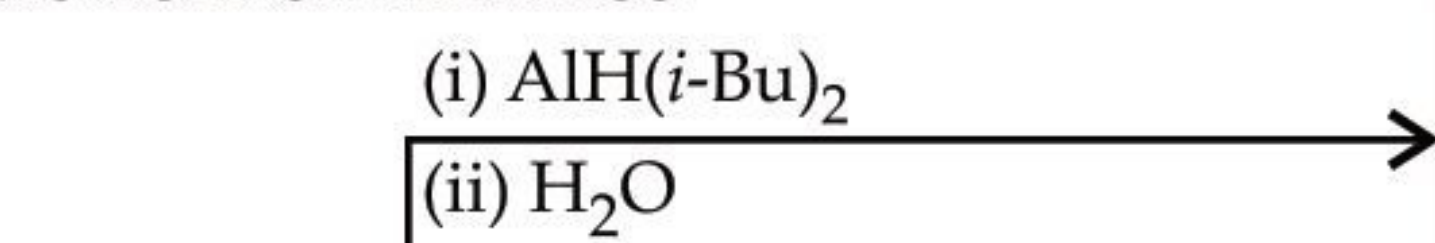
### Reductive ozonolysis of alkenes



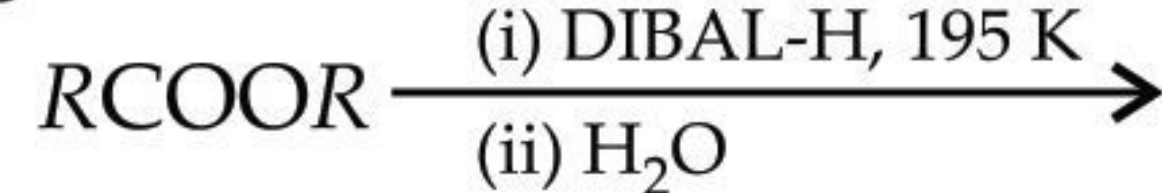
### Rosenmund reduction



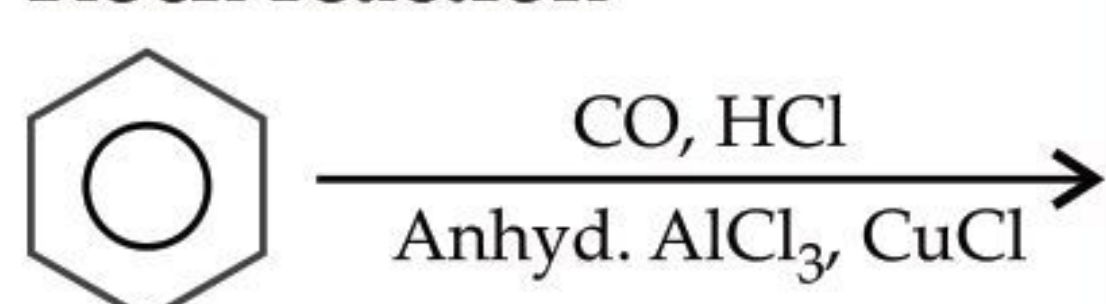
### Reduction of nitriles



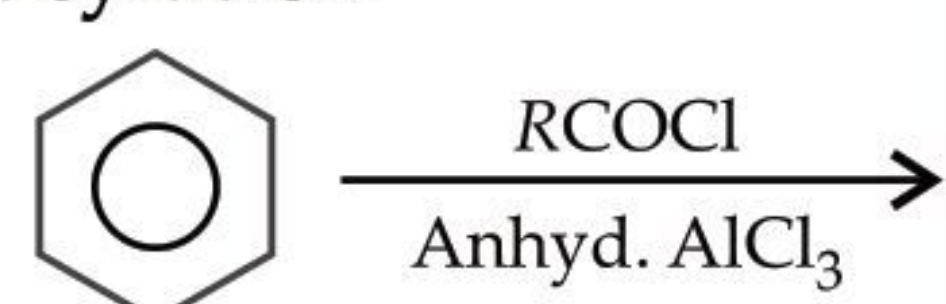
### From esters



### Gatterman-Koch reaction



### Friedel-Crafts acylation

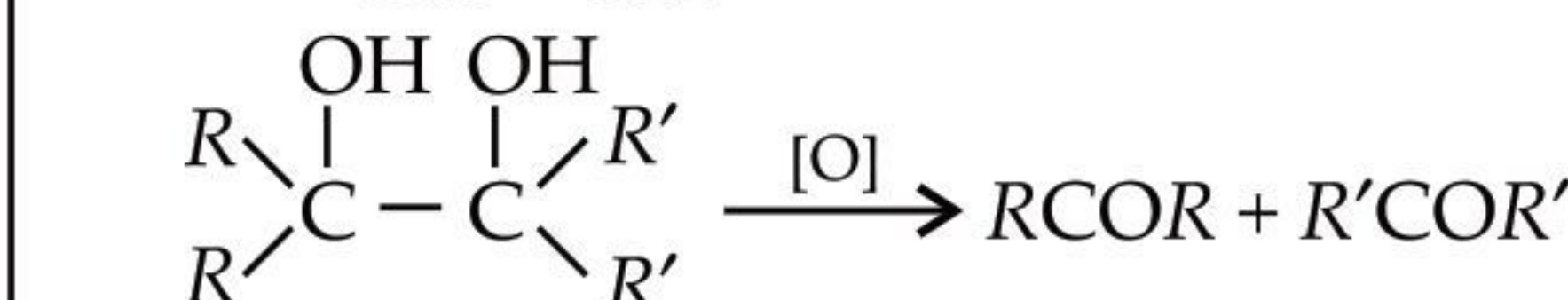


**Aldehydes  
and  
Ketones**

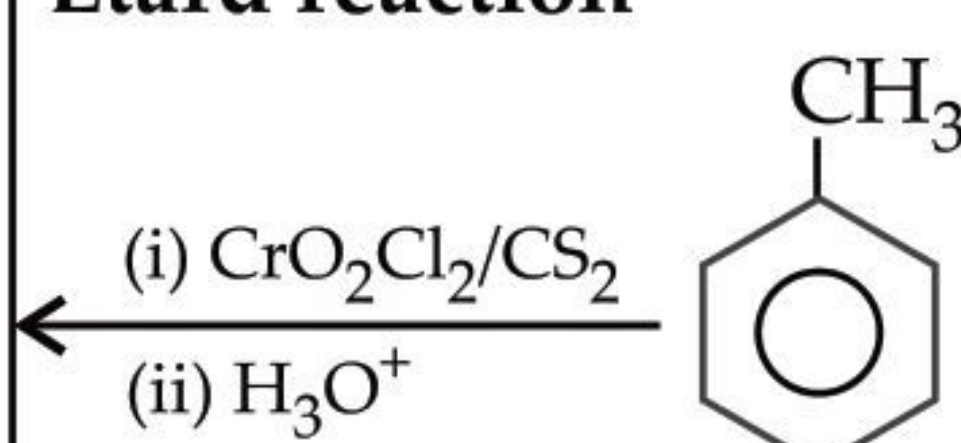
### From alkynes



### Oxidation of 1,2-glycols



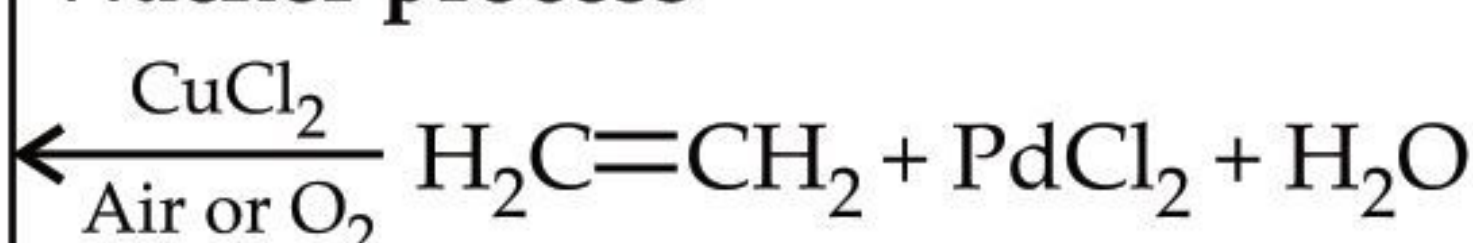
### Etard reaction



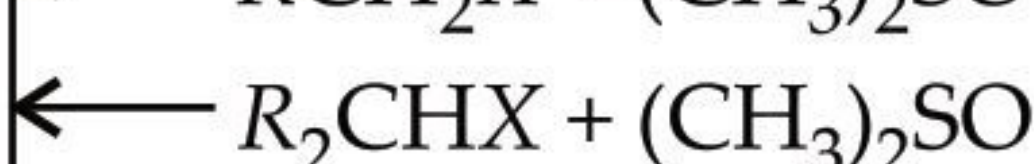
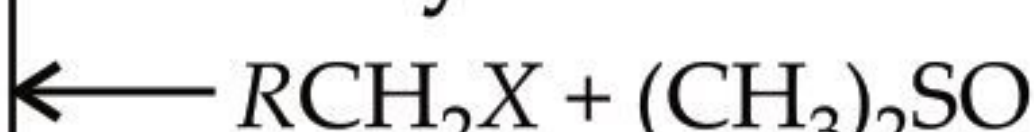
### Oxo process



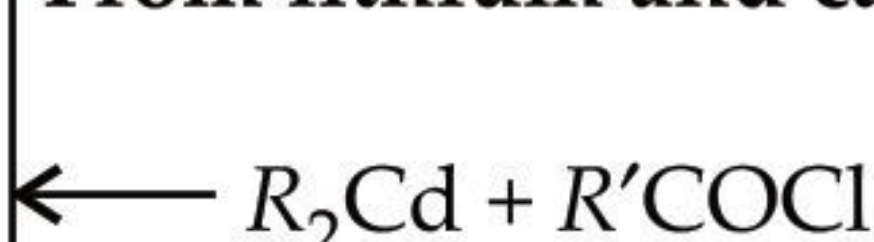
### Wacker process



### From alkyl halides

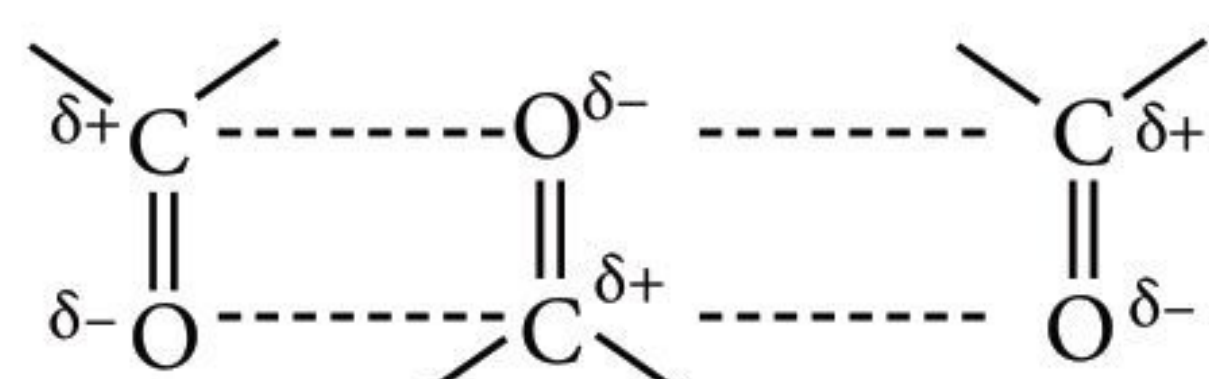


### From lithium and cadmium salts



## Physical Properties

- Carbonyl compounds are held together by dipole-dipole interactions.

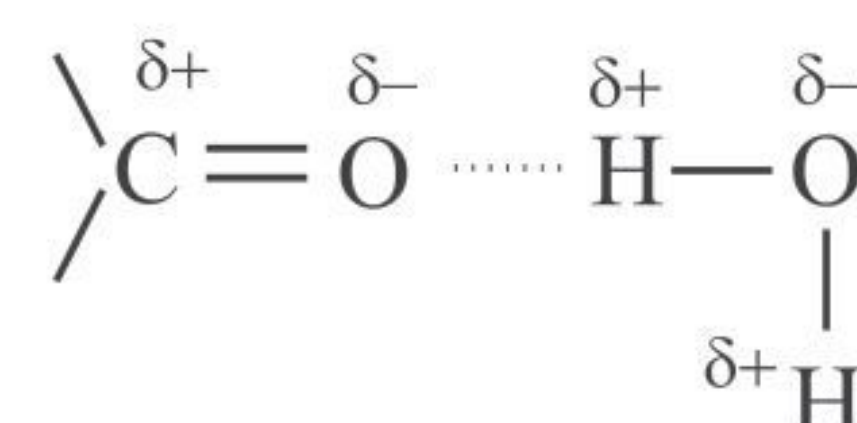


Dipole-dipole interactions are weaker forces than H-bonding and stronger than the van der Waals' interactions. Thus boiling points of aldehydes and ketones are somewhat higher than those of hydrocarbons and lower than those of alcohols of comparable molecular mass.

alcohols > carbonyl compounds > alkanes

**Note:** Among the carbonyl compounds, ketones have slightly higher boiling points than the isomeric aldehydes because of presence of two electrons releasing groups around the carbon atom of carbonyl group which makes them more polar *i.e.*, they also have more dipole moment than aldehydes.

- Lower members are water soluble as they can form hydrogen bonding with water as

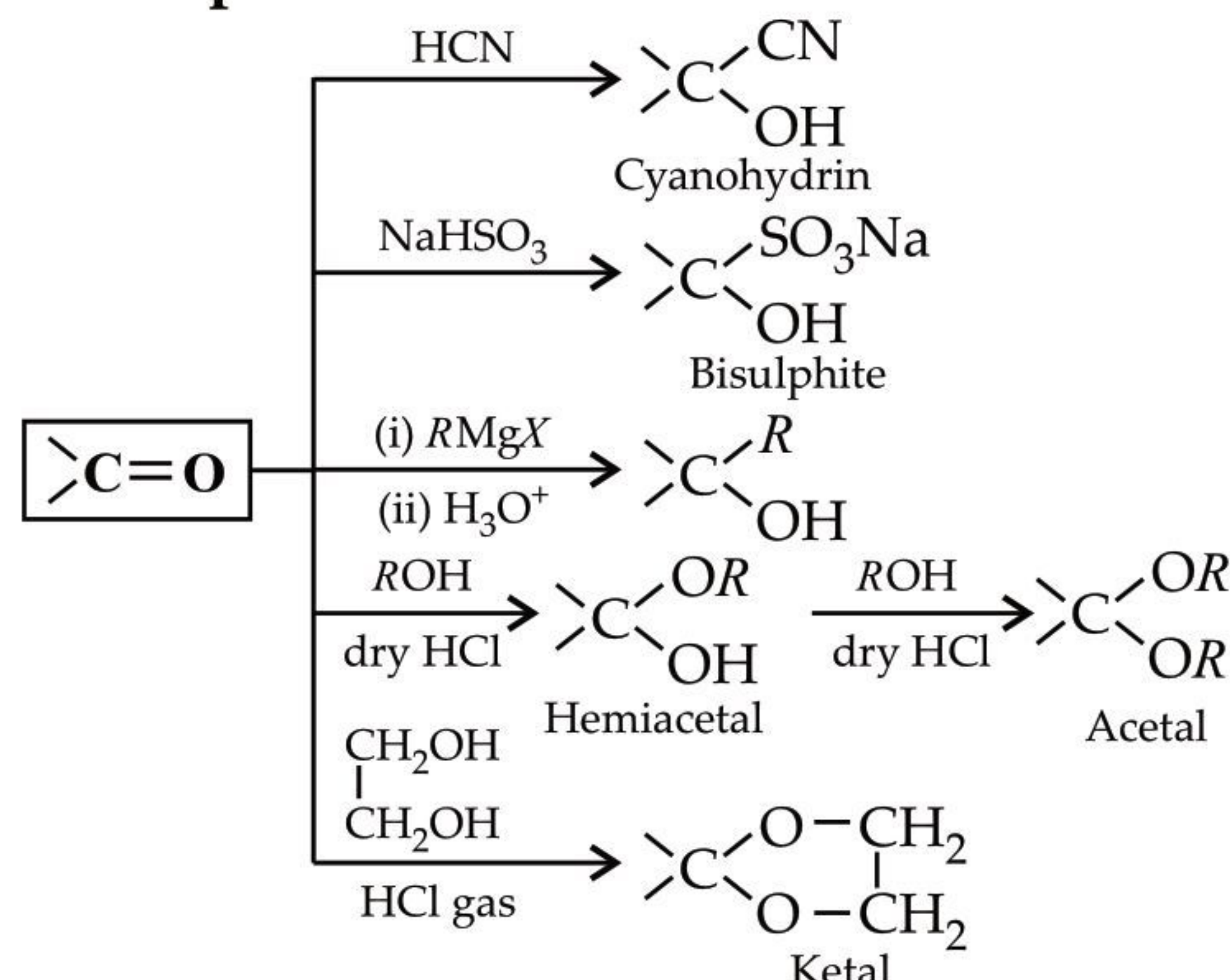


- The solubility in water decreases with increase in molecular mass.
- Carbonyl compounds have lower density than water.

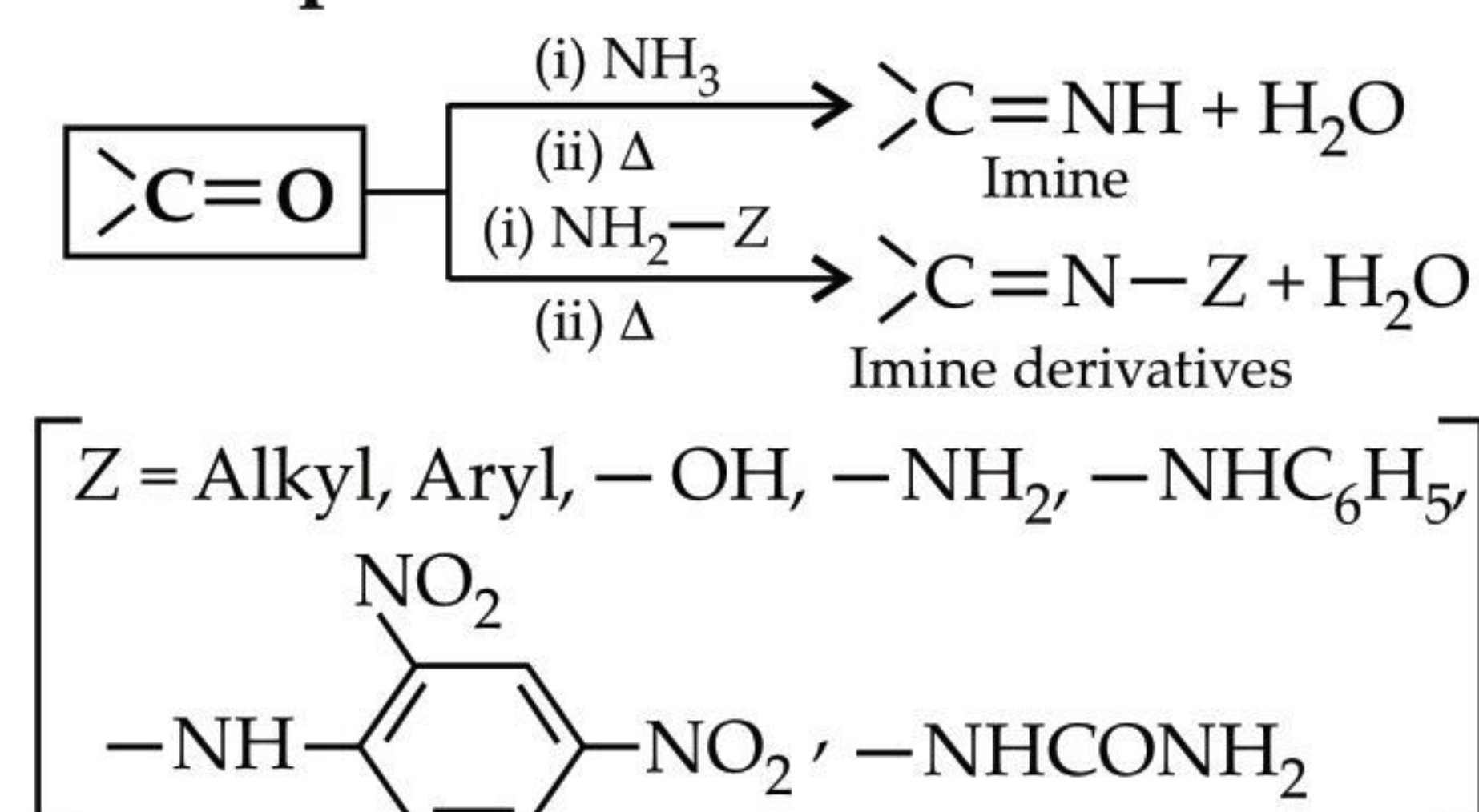


## Chemical Properties

### ◆ Nucleophilic addition reactions :

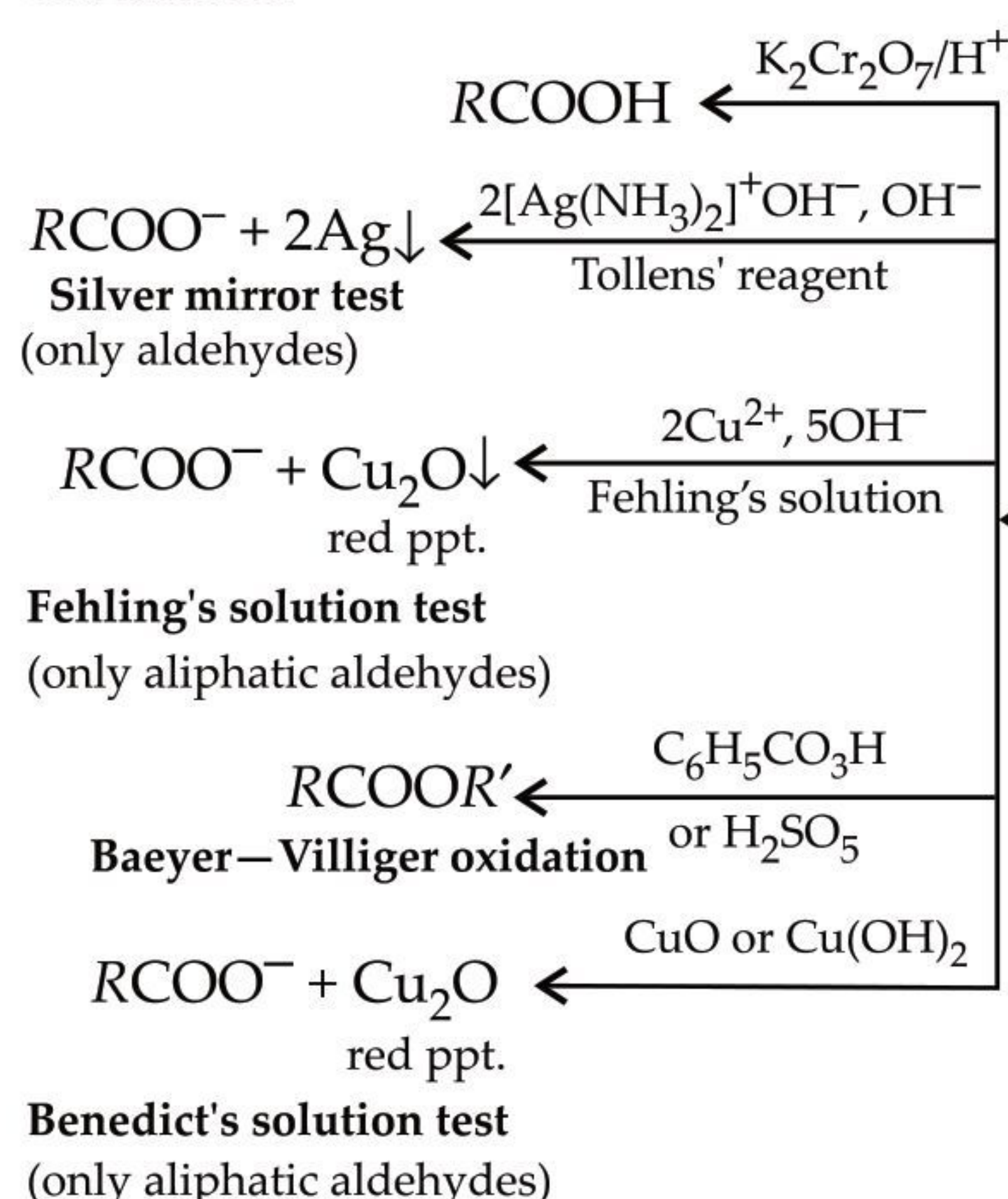


### ◆ Nucleophilic addition - elimination reactions :

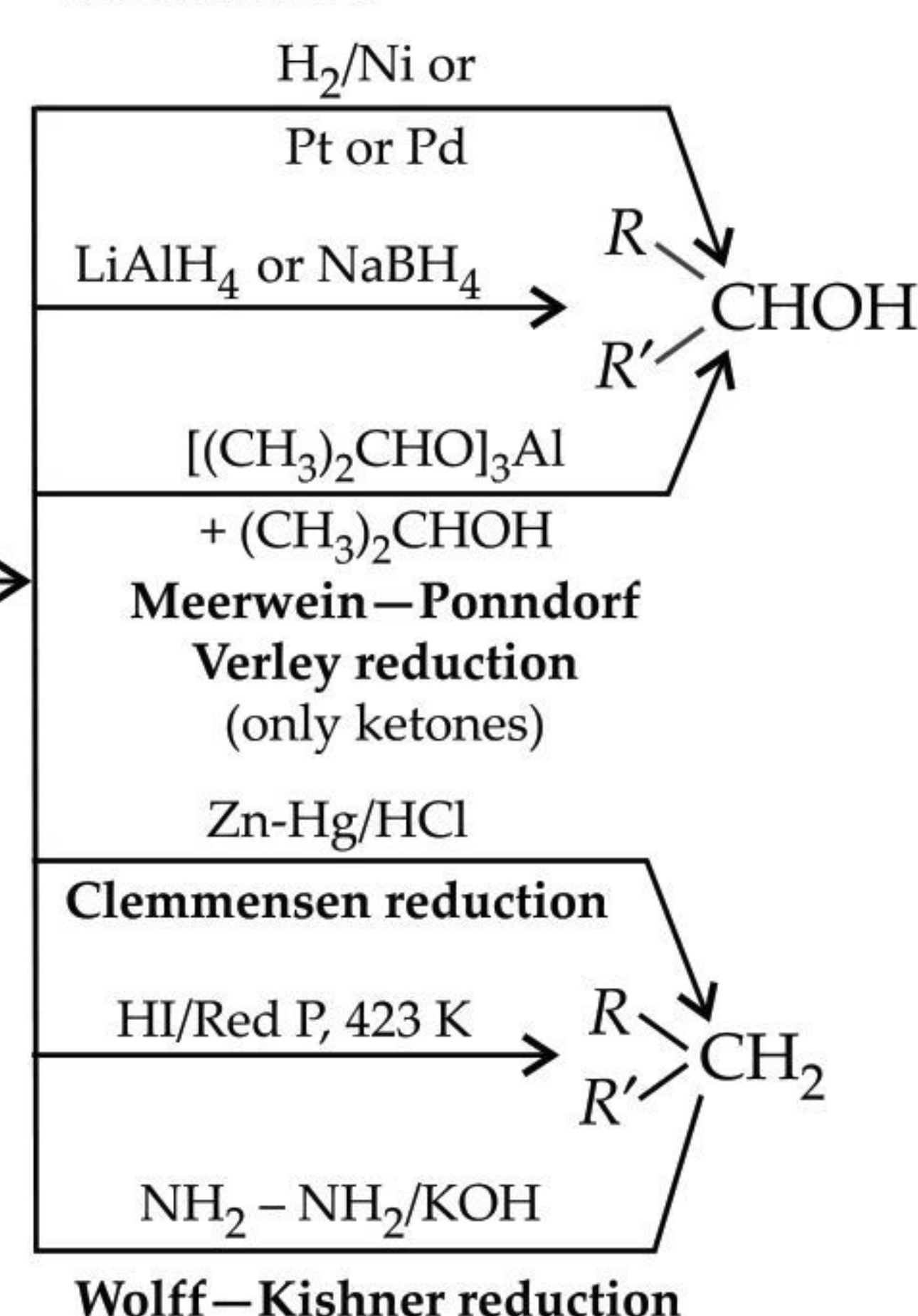


### ◆ Oxidation and reduction reactions :

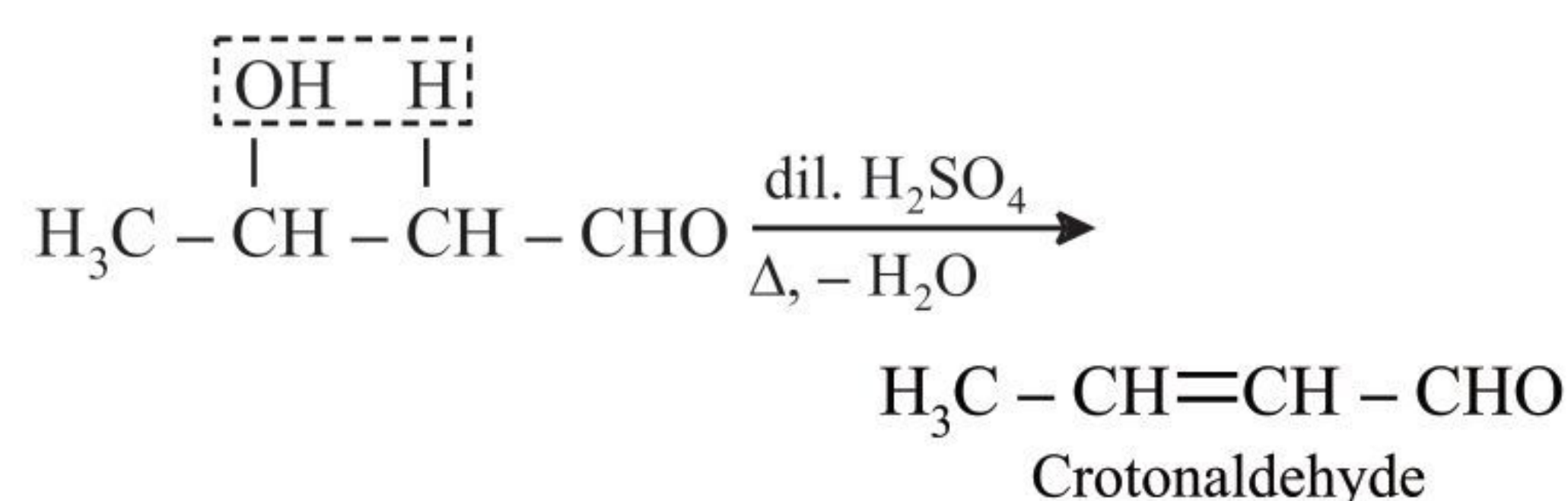
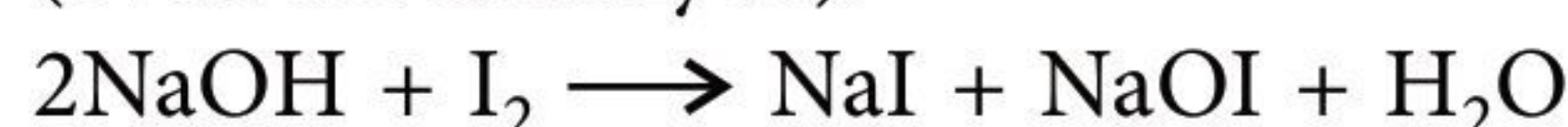
#### Oxidation



#### Reduction

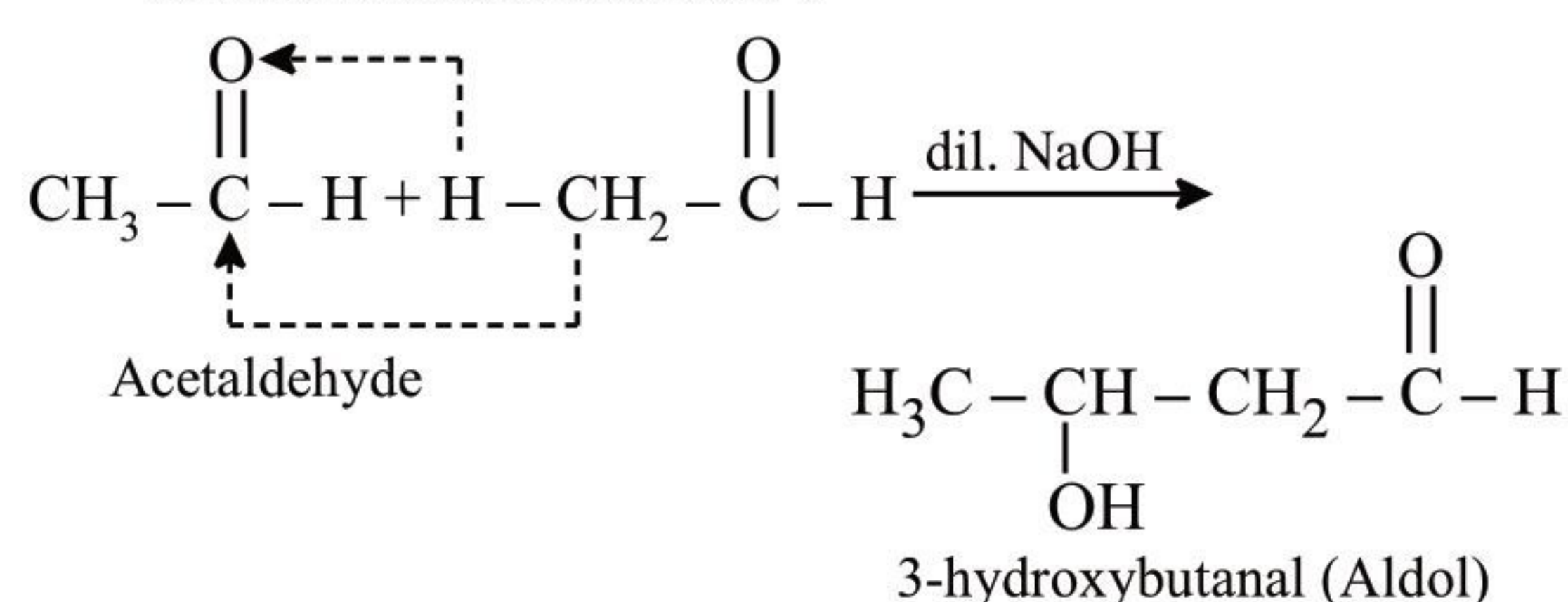


### ◆ Haloform reaction : Given by methyl ketones (even acetaldehyde).



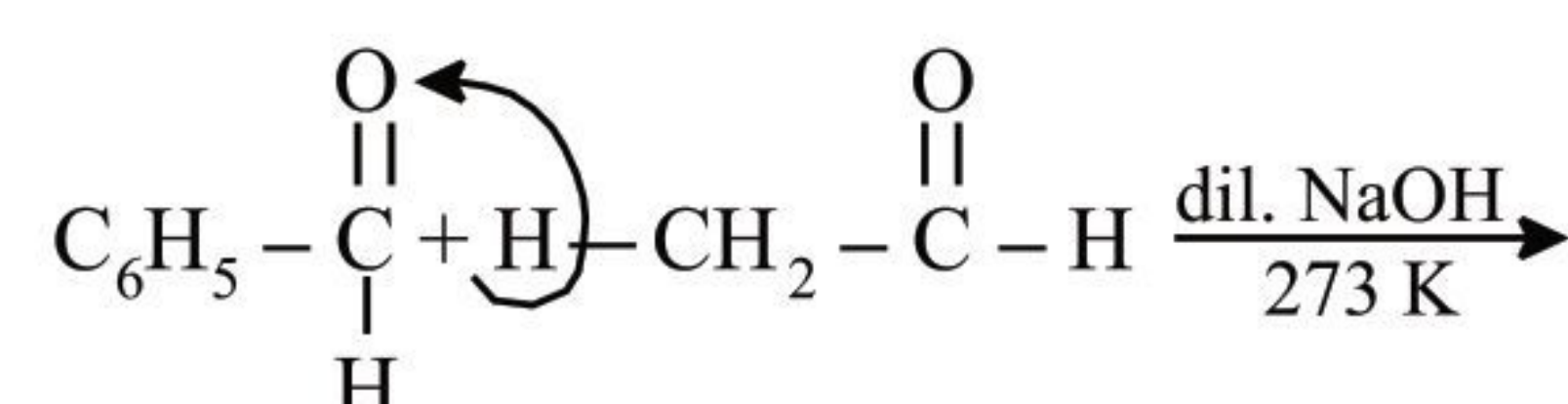
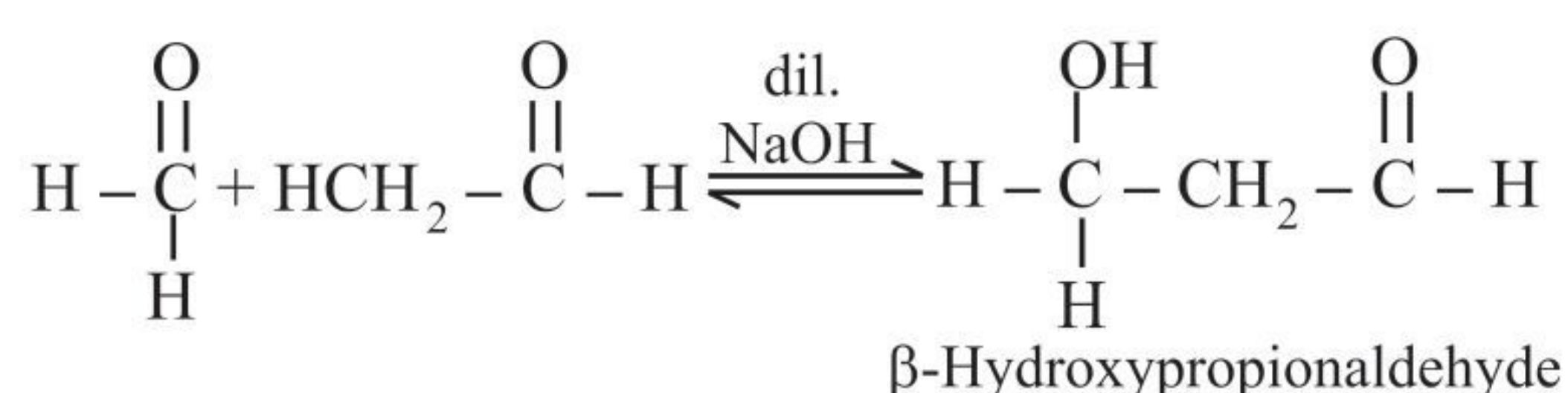
### ◆ Reactions involving α-hydrogen atom :

#### - Aldol condensation :

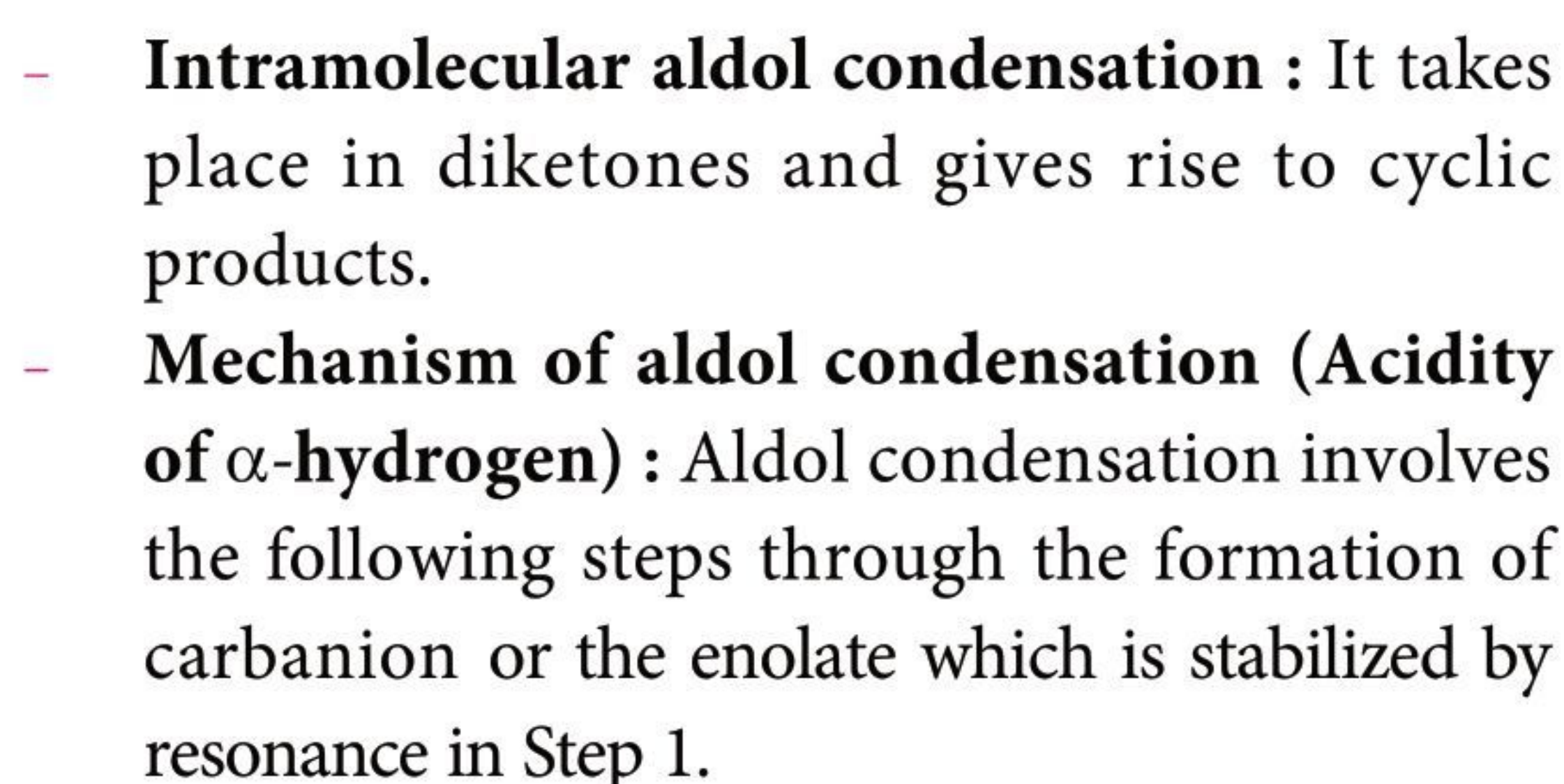
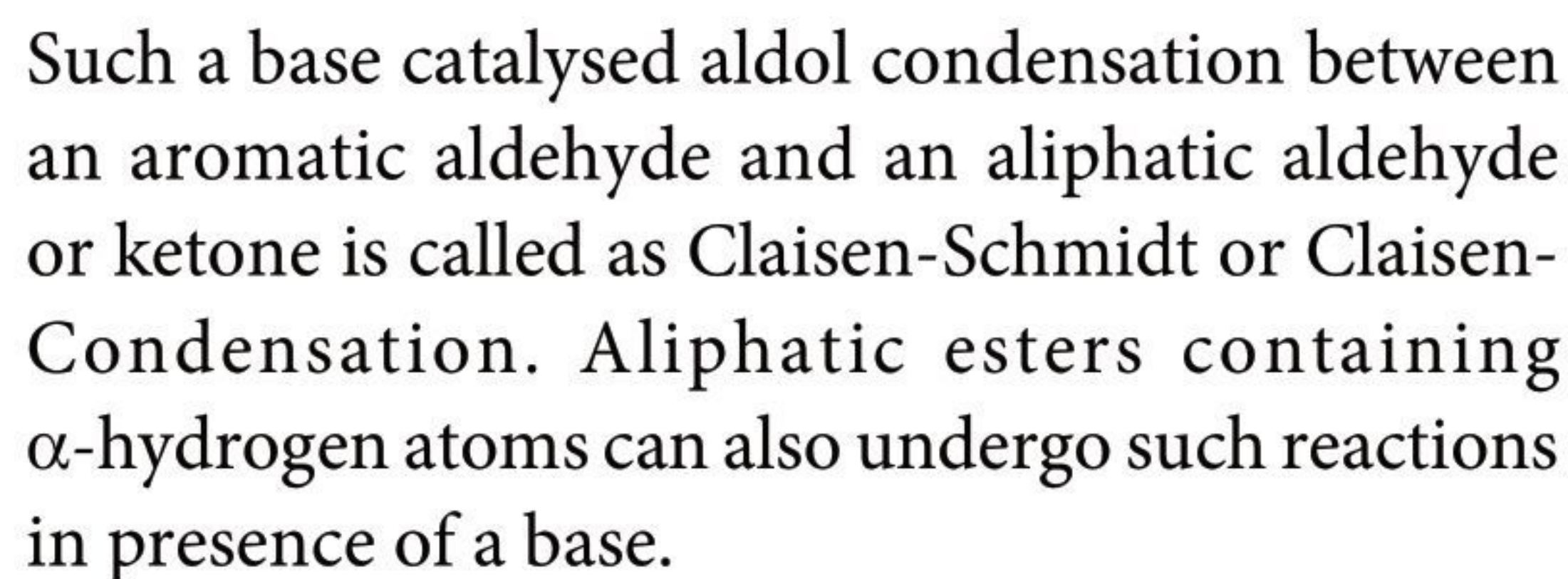
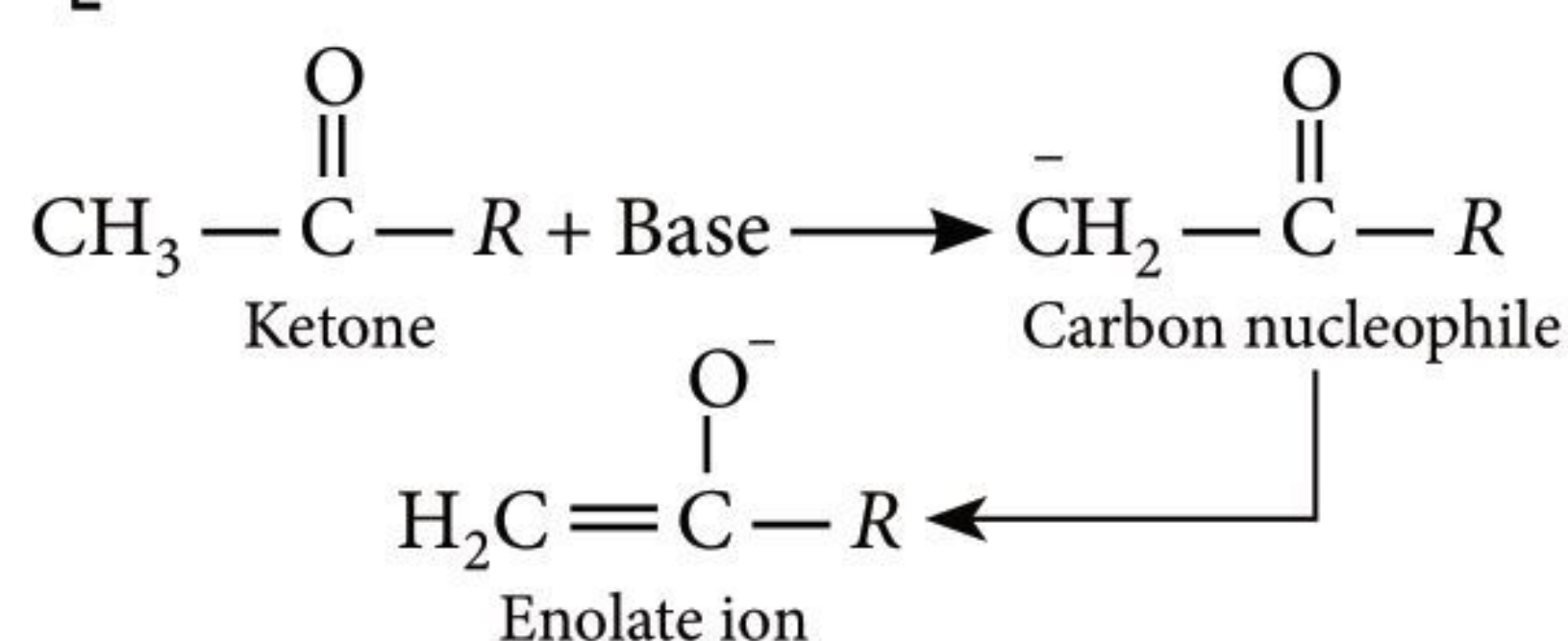


**Significance :** The products of aldol condensation on heating with dilute acid undergo dehydration to form α, β-unsaturated carbonyl compounds.

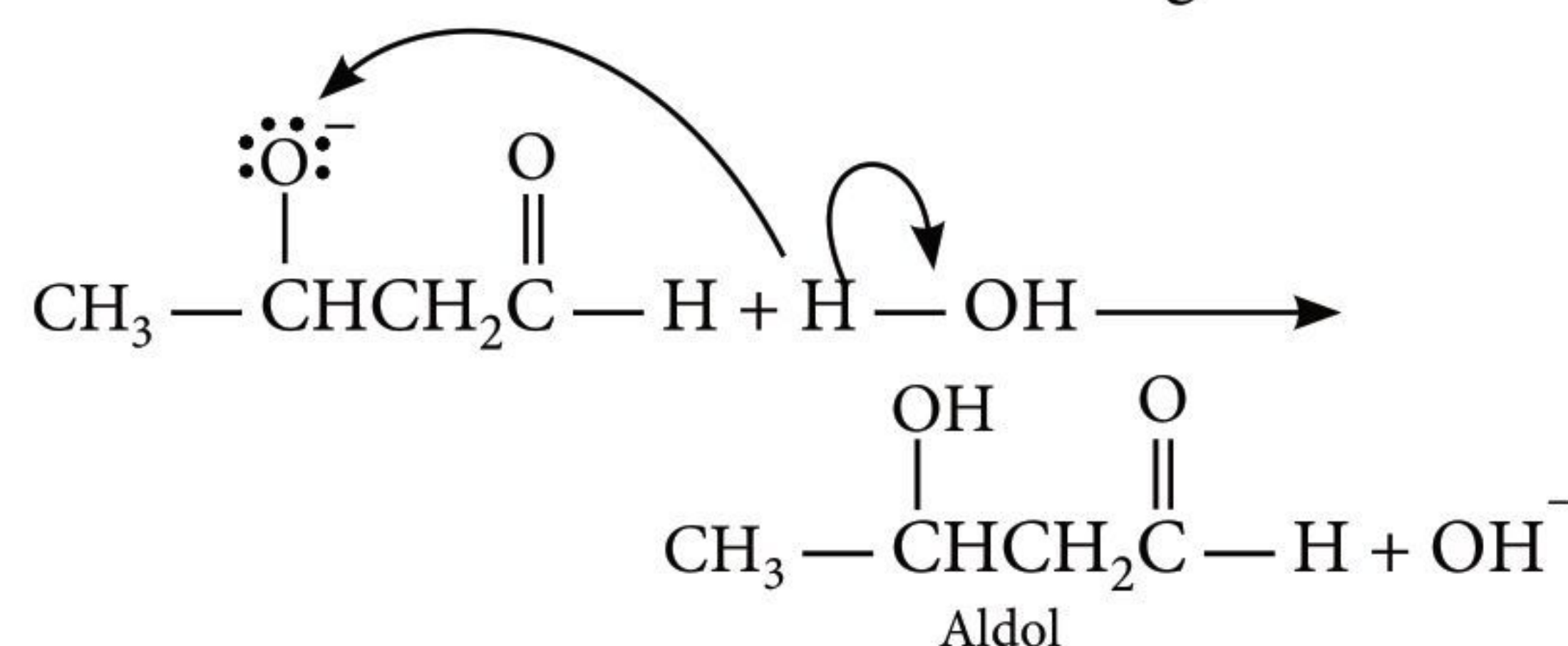
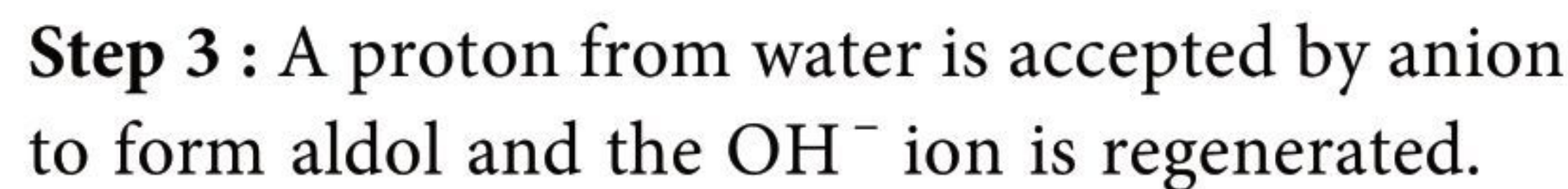
**Cross aldol condensation :** When condensation takes place between two different aldehydes or ketones, or between one aldehyde and one ketone, it is called as **cross aldol condensation**.



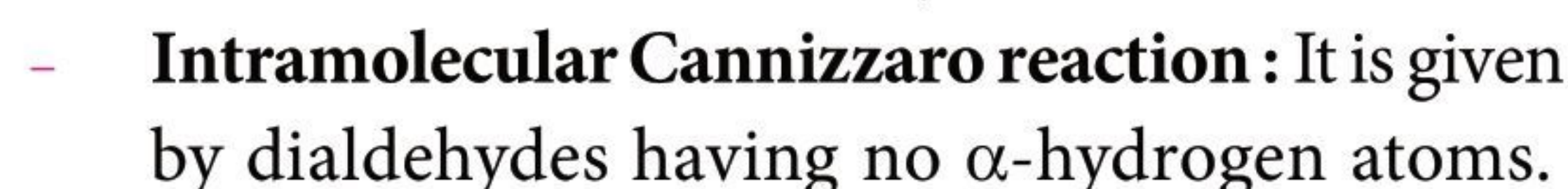



$$\begin{array}{c} \text{H} \quad \text{H} \\ | \quad | \\ \text{H}-\text{C}-\text{C}=\text{O} + \text{OH}^- \\ | \\ \text{H} \\ \text{Acetaldehyde} \end{array} \xrightleftharpoons{\text{Slow}} \text{H}_2\text{O} +$$


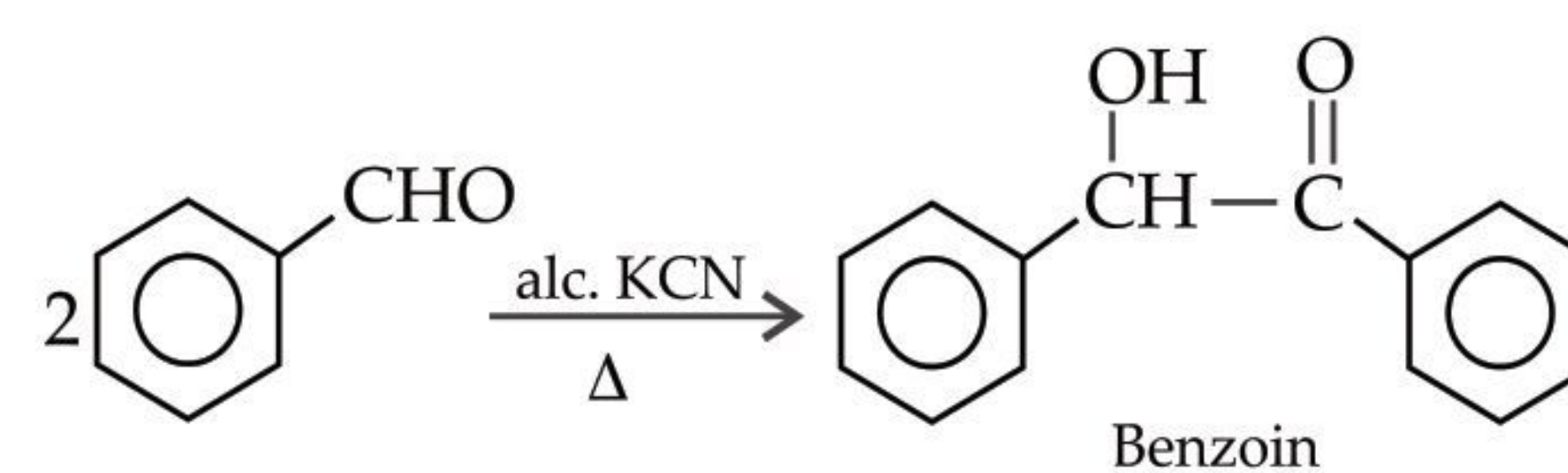
**Step 2 :** The enolate ion (nucleophile) attacks the carbonyl carbon of another aldehyde molecule to form the anion.



- **Cannizzaro reaction :**



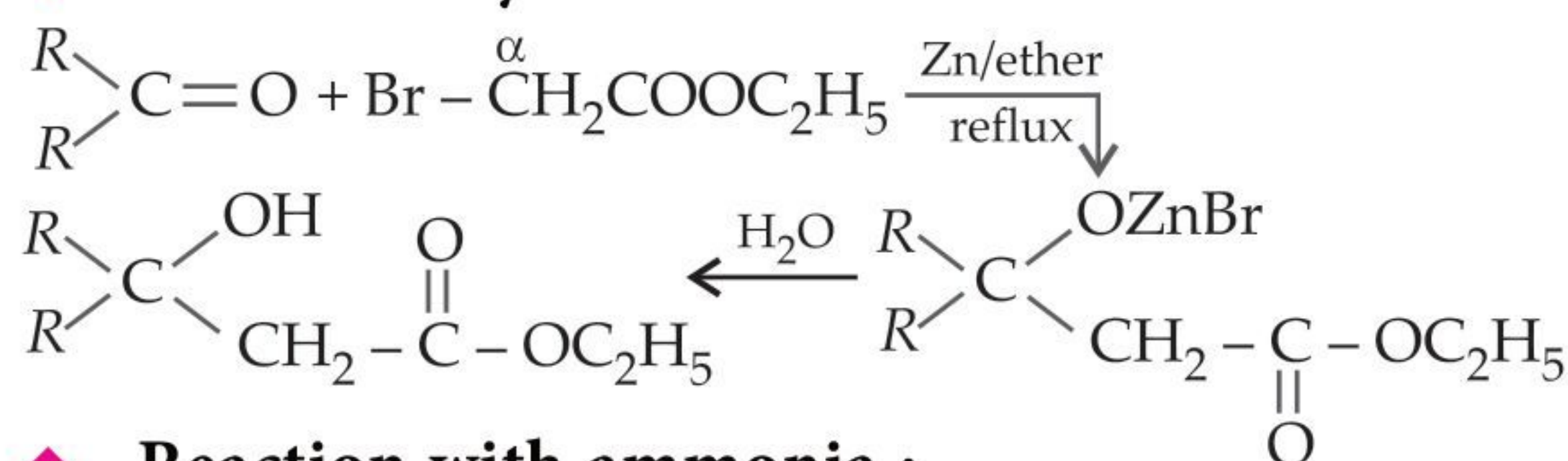
- **Tischenko's reaction :**

O=Cc1ccccc1.O=[N+]([O-])O.OS(=O)(=O)(O)O>>O=Cc1cccc([N+](=O)[O-])c1

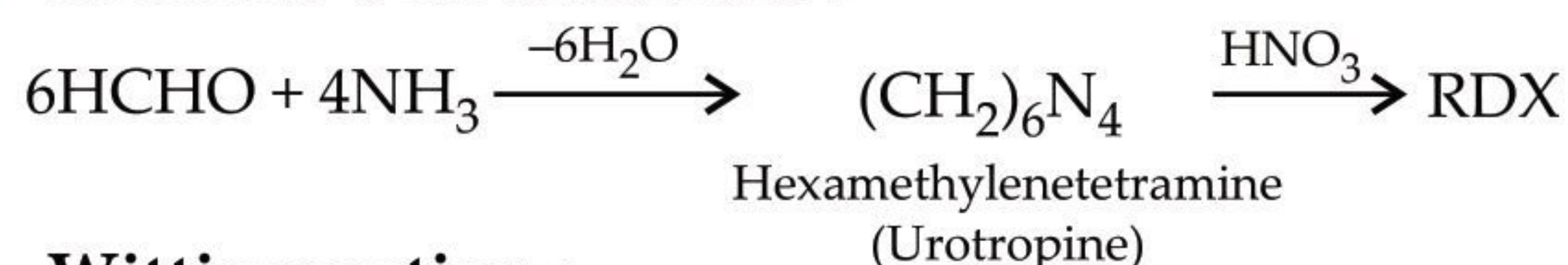
Benzaldehyde  $\xrightarrow[273-283\text{ K}]{\text{HNO}_3/\text{H}_2\text{SO}_4}$  *m*-Nitrobenzaldehyde



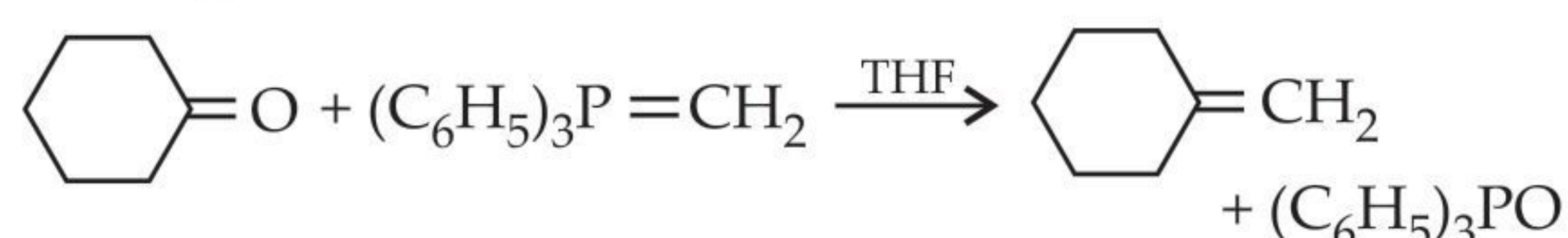
◆ **Reformatsky reaction :**



◆ **Reaction with ammonia :**



◆ **Wittig reaction :**



◆ **Distinction between aldehydes and ketones :**

Tests with	Aldehydes	Ketones
Schiff's reagent	Pink colour	No colour
Fehling's solution	Red precipitate	No precipitate
Tollens' reagent	Black precipitate of silver or silver mirror	No black ppt. or silver mirror

**Uses**

- ◆ Formaldehyde is freely soluble in water. Its 40% solution in water is sold in market under the name formalin. Formaldehyde in the form of formalin (40% formaldehyde, 8% methanol and 52% water) is used for preserving biological specimens.
- ◆ It is also used in the manufacture of synthetic polymers like bakelite and synthetic dye stuffs like indigo.
- ◆ Acetaldehyde is used in the commercial preparation of a number of organic compounds such as acetic acid, ethyl acetate, *n*-butyl alcohol, etc.
- ◆ Paraldehyde is used in medicines as a hypnotic.
- ◆ Benzaldehyde is an important flavouring agent in perfume industry.
- ◆ It is used in manufacture of dyes like malachite green.
- ◆ Acetone is very important solvent and is extensively used as a solvent in industries and laboratories.
- ◆ It is used in the manufacture of thermosoftening plastic (Perspex).
- ◆ It is used as one of the constituents of liquid nail polish.

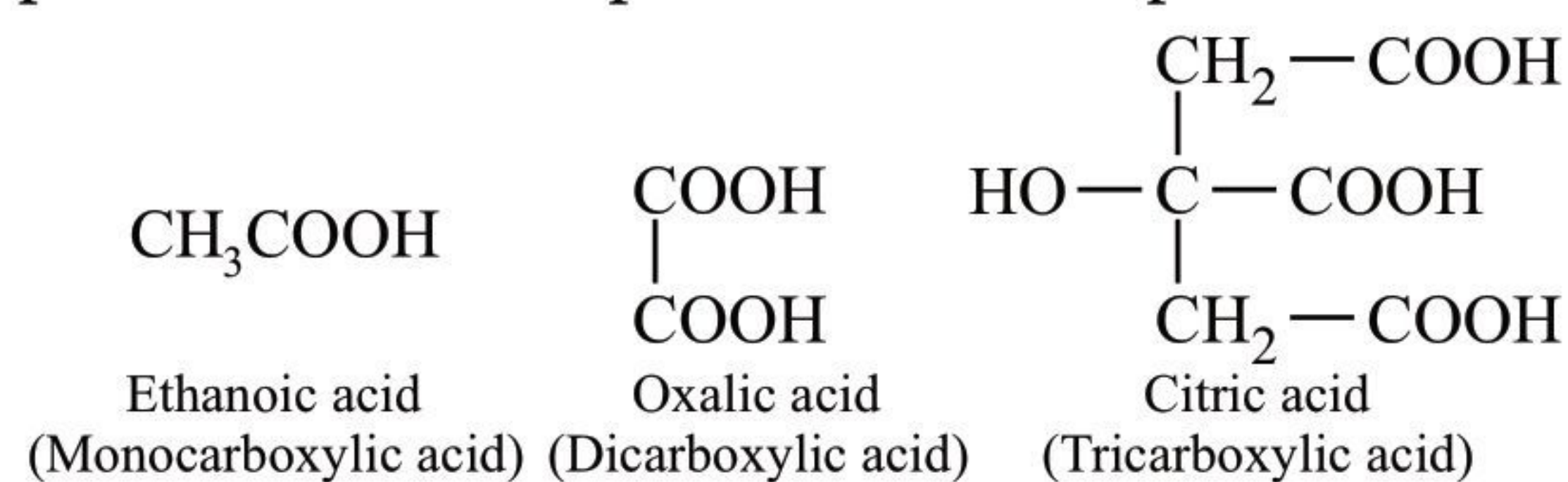
**CARBOXYLIC ACIDS**

- ◆ Compounds containing  $-COOH$  group having general formula  $C_nH_{2n}O_2$ .

- ◆ Carboxylic functional group ( $-COOH$ ) may be considered as a combination of carbonyl group ( $>C=O$ ) and hydroxyl group ( $-OH$ ).

**Nomenclature**

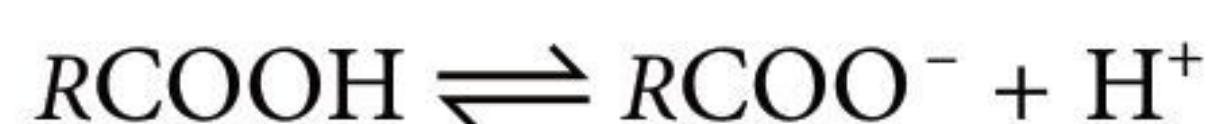
- ◆ The common names end with the suffix *-ic acid* and have been derived from Latin or Greek names of their natural sources.
- ◆ In the IUPAC system, aliphatic carboxylic acids are named by replacing the ending *-e* in the name of the corresponding alkane with *-oic acid*.
- ◆ Carboxylic acids may be mono-, di-, or tri- carboxylic acids depending on the number of carboxyl groups present in the compound. For example,



- ◆ Carboxylic acids may be aliphatic or aromatic depending on whether the  $-COOH$  group is attached to an alkyl or aryl group respectively. Higher members of aliphatic monocarboxylic acids ( $C_{12}-C_{17}$ ) are also known as *fatty acids* since they occur in fats as glycerides.

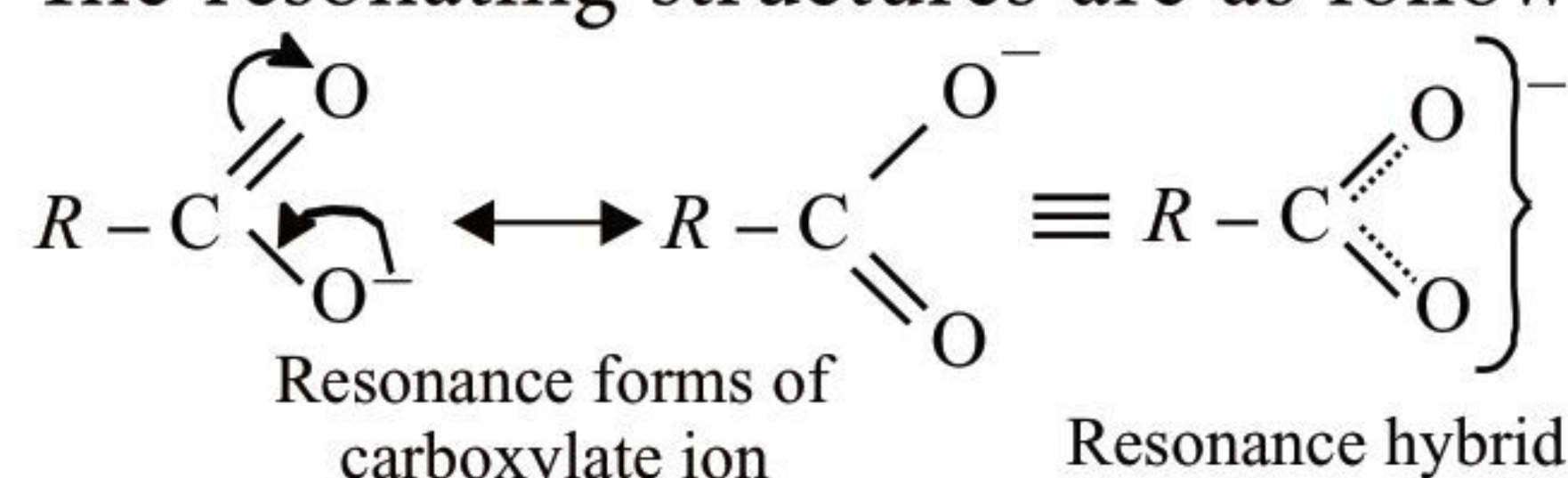
**Acidity of Carboxylic Group**

- ◆ The acidic character of carboxylic acids is due to release of  $H^+$  ion in aqueous solution.



This is explained with the help of resonance of carboxylate ion.

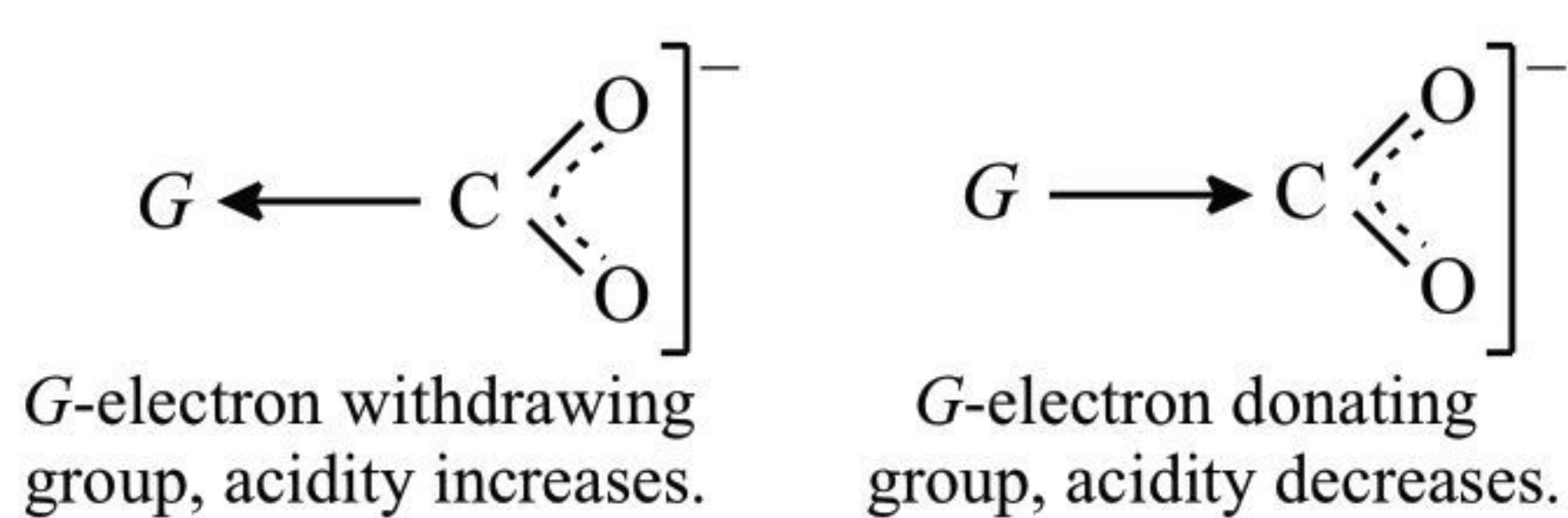
The resonating structures are as follows :



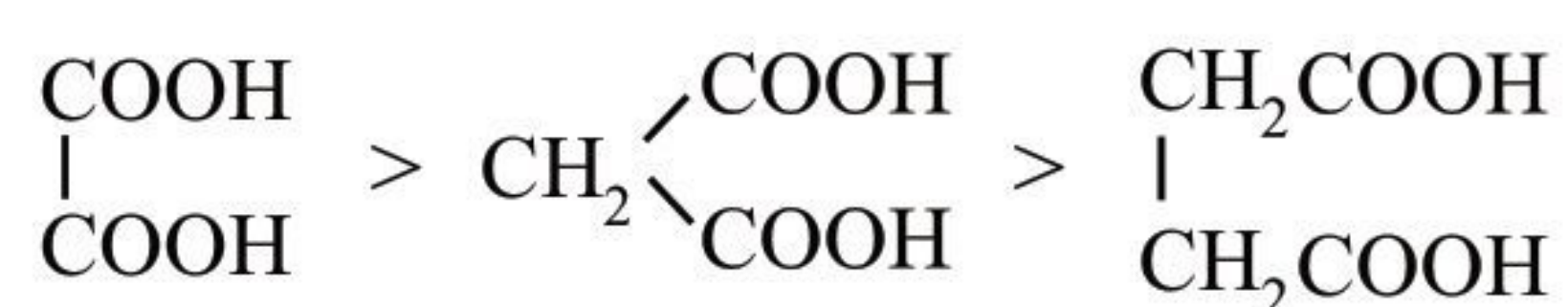
Due to electronegativity of oxygen atom, it attracts the electrons of the  $O-H$  bond towards itself. This helps in release of hydrogen as proton. Thus, the acidity of carboxylic acid is due to powerful resonance stabilization of the anion.

- ◆ **Effect of substituents on acidity :** An electron withdrawing substituent having  $-I$  effect stabilizes the anion by dispersing the negative charge and therefore, increases the acidity. On the other hand, electron releasing substituents having  $+I$  effect intensify the negative charge on the anion resulting in the decrease of stability of the anion and thus decrease the acidity of the acid.



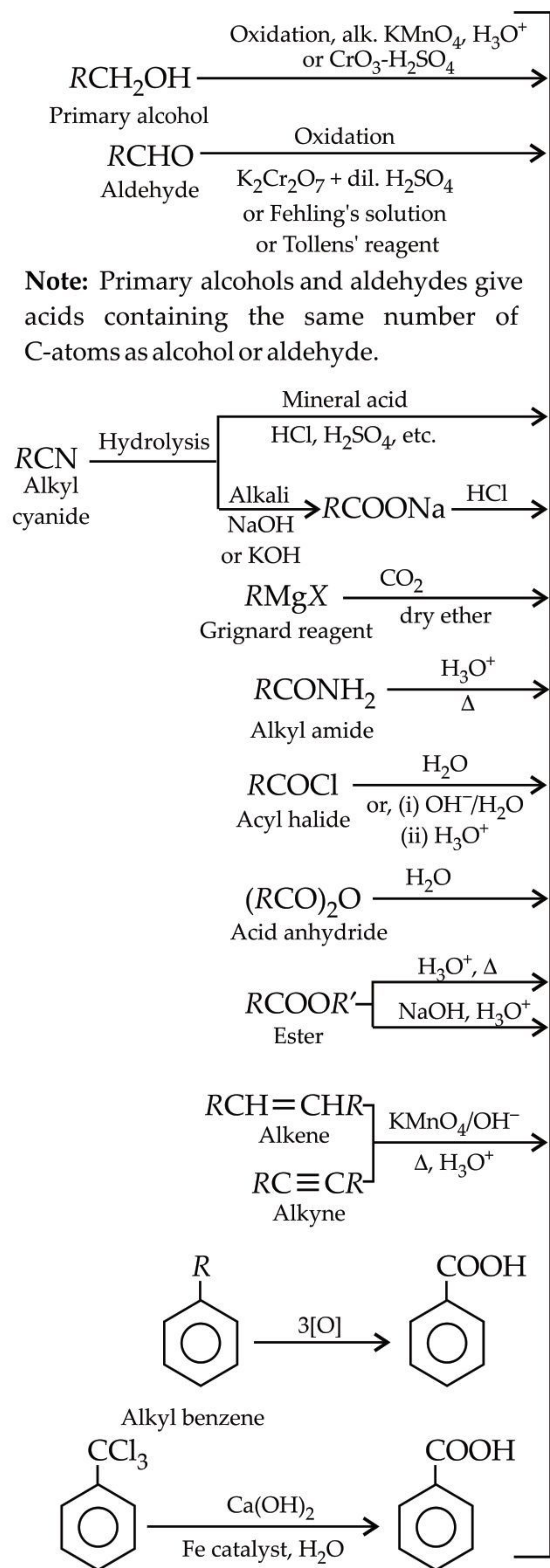


Hence the following sequence is observed :

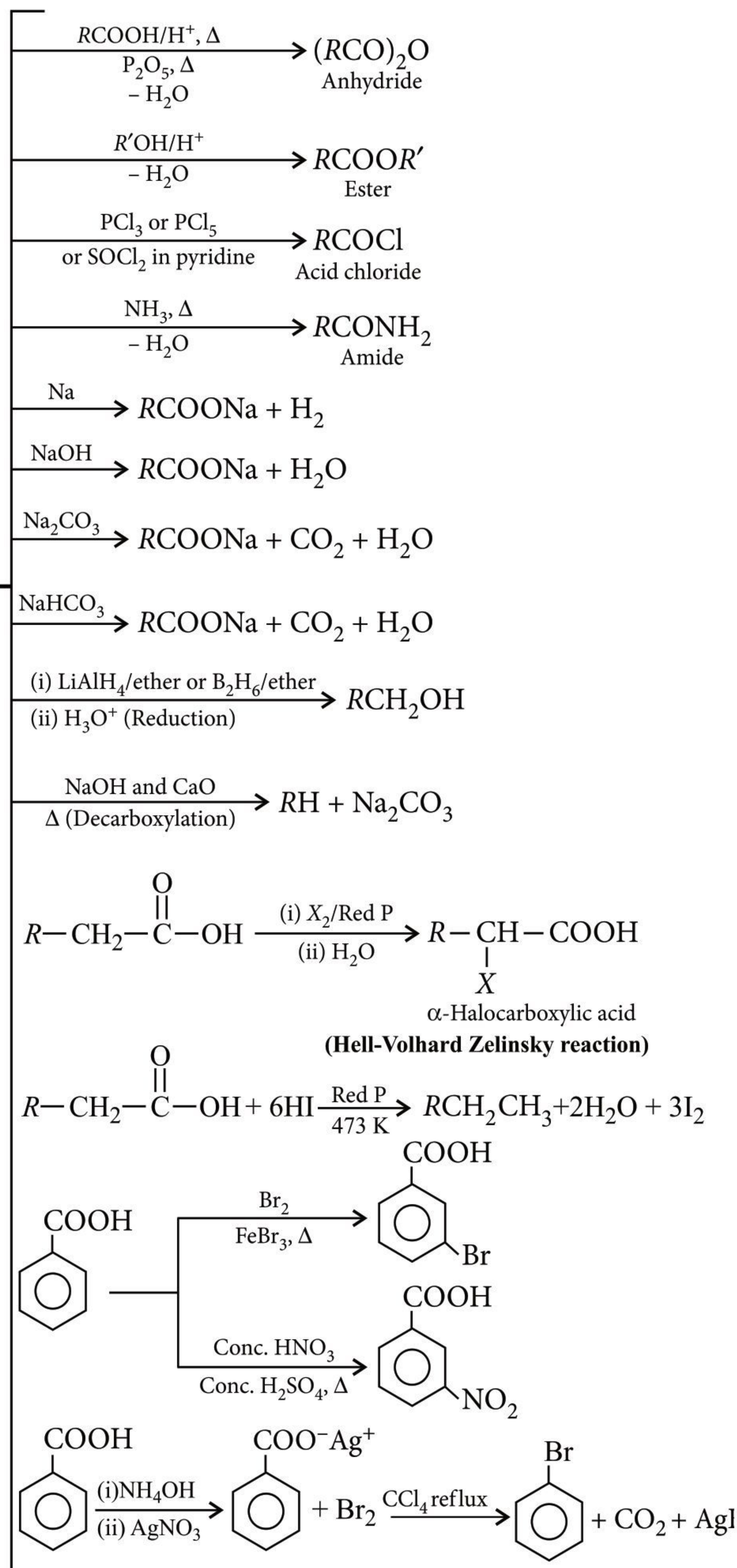


## Methods of Preparation and Chemical Properties

### Preparation



### Chemical Properties





## Physical Properties

- ◆ **Physical state** : First three members are colourless liquids with pungent smell. The next six are oily liquids with faint unpleasant smell. Others are colourless waxy solids. Benzoic acid and its homologues are colourless solids.
- ◆ **Solubility** : Lower carboxylic acids are soluble in water and higher members are insoluble. First four members are very soluble in water. Benzoic acid is sparingly soluble in cold water but is soluble in alcohol, ether, etc. It is also soluble in hot water.
- ◆ **Boiling points** : They have higher boiling point due to presence of hydrogen bonding and in case of monocarboxylic acids it increases with increase in molecular mass.
- ◆ **Melting points** : The melting point increases irregularly with increase in molecular mass. The melting point of carboxylic acids with even number of carbon atom is higher than the next lower and higher member containing odd number of carbon atoms. The m.p. and b.p. of aromatic acids are generally higher than those of aliphatic acids of comparable molecular mass.
- ◆ **Distinction between phenol and carboxylic acid** :

Test	Phenol	Carboxylic acid
NaHCO <sub>3</sub> test	No reaction	Brisk effervescence of CO <sub>2</sub> gas
FeCl <sub>3</sub> test	Violet colour	Buff coloured ppt.

## Uses

- ◆ Methanoic acid is used
  - In leather tanning.
  - As coagulating agent for rubber latex in rubber industry.
  - In textile dyeing and finishing.
  - In the manufacture of rayon and in plastic, rubber and silk industries.
- ◆ Ethanoic acid is used as vinegar in cooking and in food industry.
- ◆ Benzoic acid is used
  - Sodium salts of benzoic acid is used as a food preservative.
  - Its esters are used in perfumery.

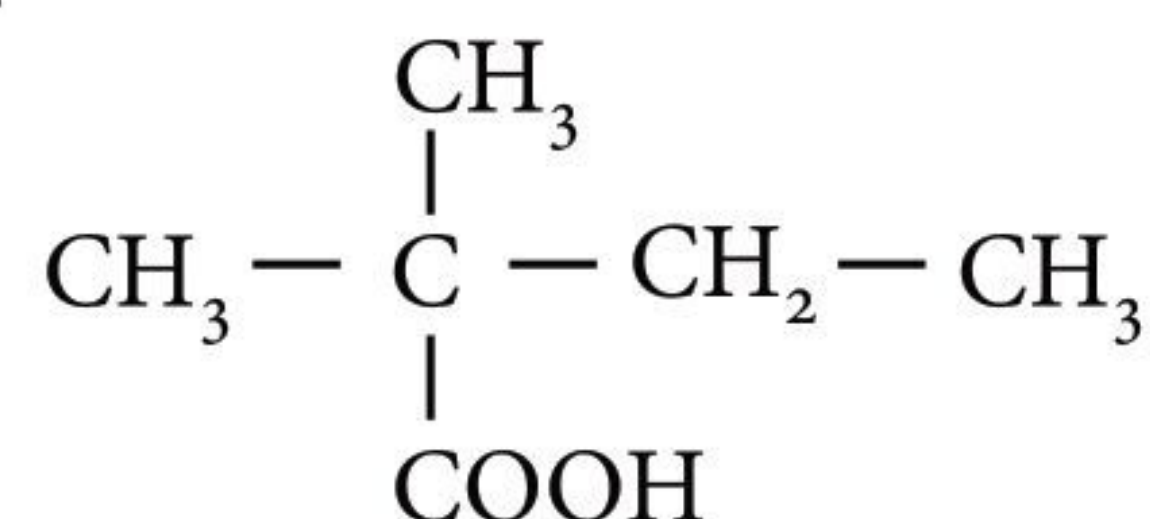
## Questions for Practice

1. Draw the structures of the following :
  - (i) *p*-Methylbenzaldehyde
  - (ii) 4-Methylpent-3-en-2-one(AI 2015C)

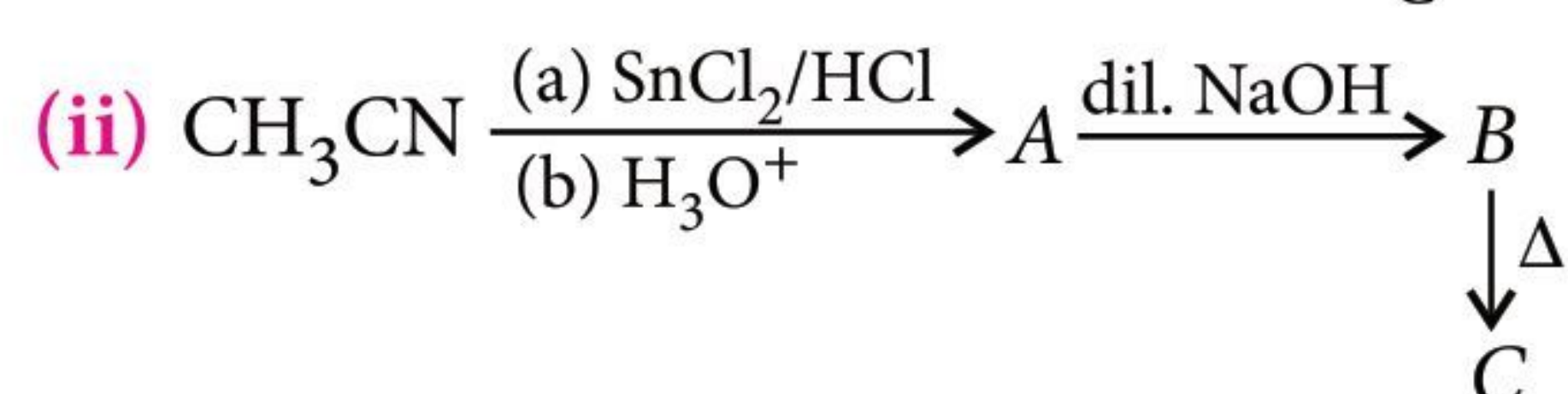
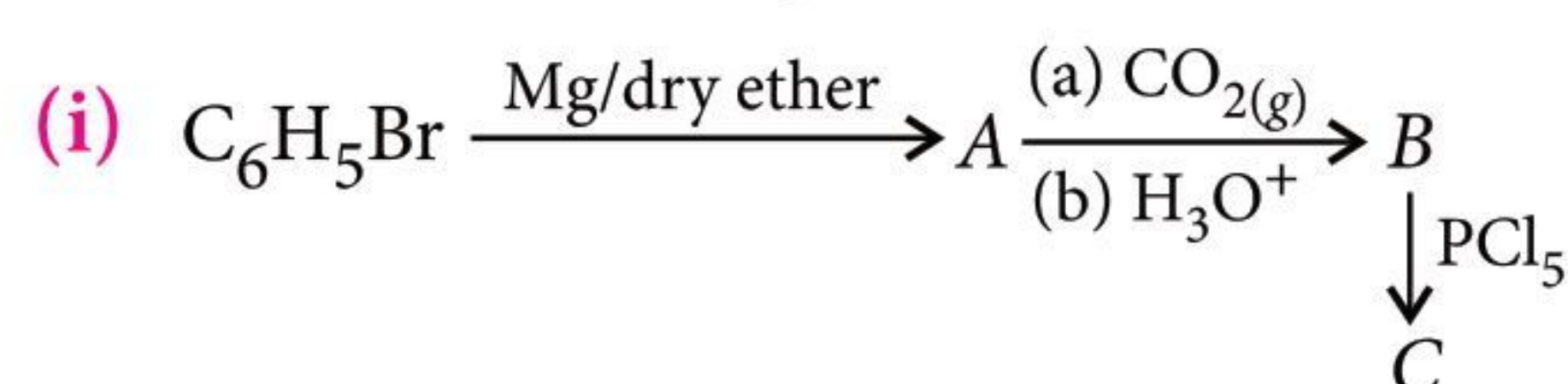
2. Write chemical equations for the following reactions :
  - (i) Propanone is treated with dilute Ba(OH)<sub>2</sub>.
  - (ii) Acetophenone is treated with Zn(Hg)/Conc. HCl(Delhi 2019)

3. (a) Write the chemical reaction involved in Wolff-Kishner reduction.  
(b) Arrange the following in the increasing order of their reactivity towards nucleophilic addition reaction.  
C<sub>6</sub>H<sub>5</sub>COCH<sub>3</sub>, CH<sub>3</sub>—CHO, CH<sub>3</sub>COCH<sub>3</sub>  
(c) A and B are two functional isomers of compound C<sub>3</sub>H<sub>6</sub>O. On heating with NaOH and I<sub>2</sub>, isomer B forms yellow precipitate of iodoform whereas isomer A does not form any precipitate. Write the formulae of A and B. (AI 2016)

4. What is the correct IUPAC name of the given compound?



- (a) 2,2-Dimethylbutanoic acid
  - (b) 2-Carboxyl-2-methylbutane
  - (c) 2-Ethyl-2-methylpropanoic acid
  - (d) 3-Methylbutanecarboxylic acid
- (2020)
- 
5. Arrange the following in the increasing order of their boiling points.  
CH<sub>3</sub>CHO, CH<sub>3</sub>COOH, CH<sub>3</sub>CH<sub>2</sub>OH  
(AI 2016, 2015)
  6. Write the structures of compounds A, B and C in each of the following reactions :



(Delhi 2017)

## AMINES

These are alkyl or aryl derivatives of ammonia and are obtained by replacing one, two or three hydrogen atoms by alkyl/aryl groups.

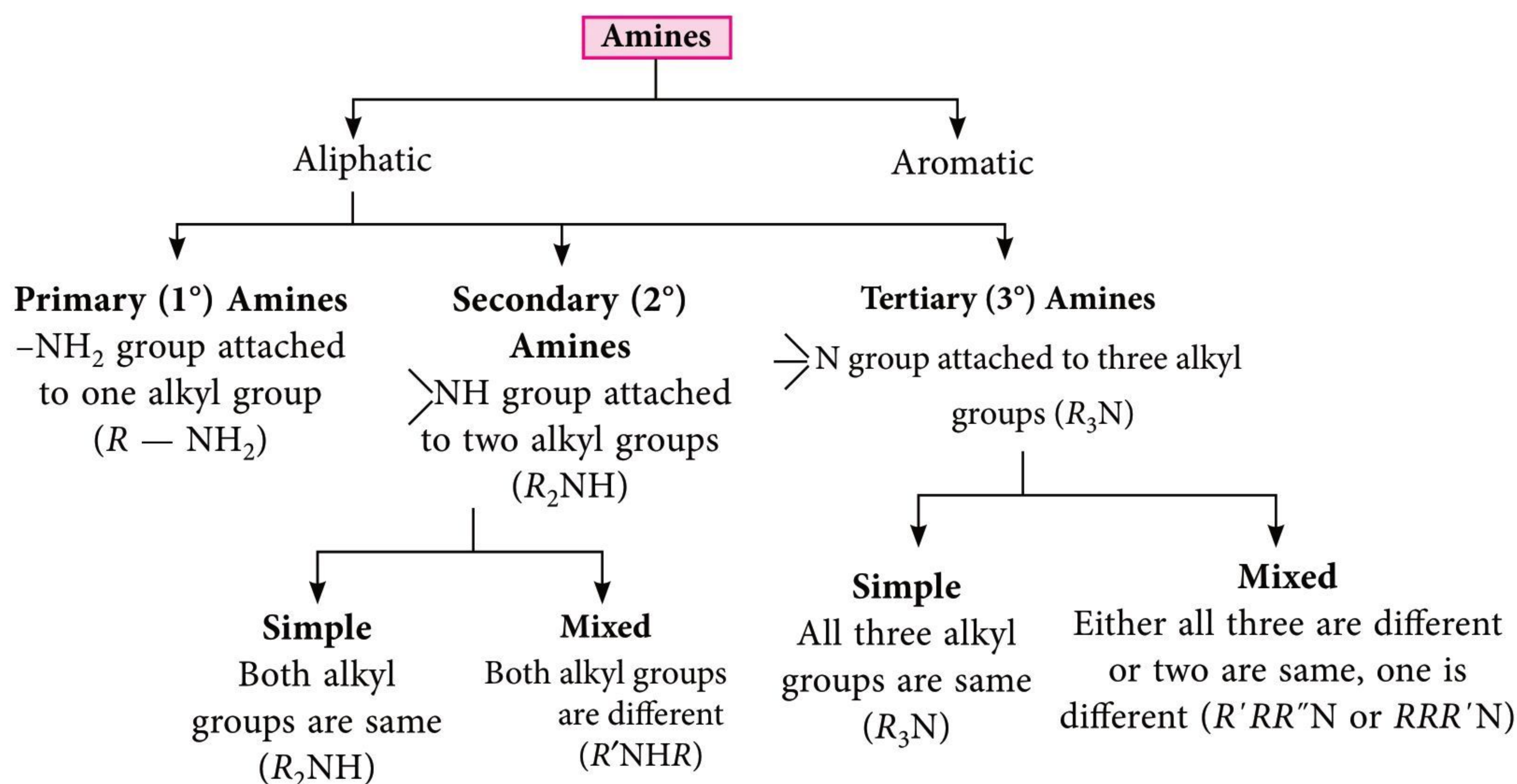
## Nomenclature

In common system, an aliphatic amine is named by prefixing alkyl group to amine, i.e., *alkylamine*. In IUPAC



system, amines are named as *alkanamines*. In secondary and tertiary amines, when two or more groups are the same, the prefix *di* or *tri* is appended before the name of alkyl group.

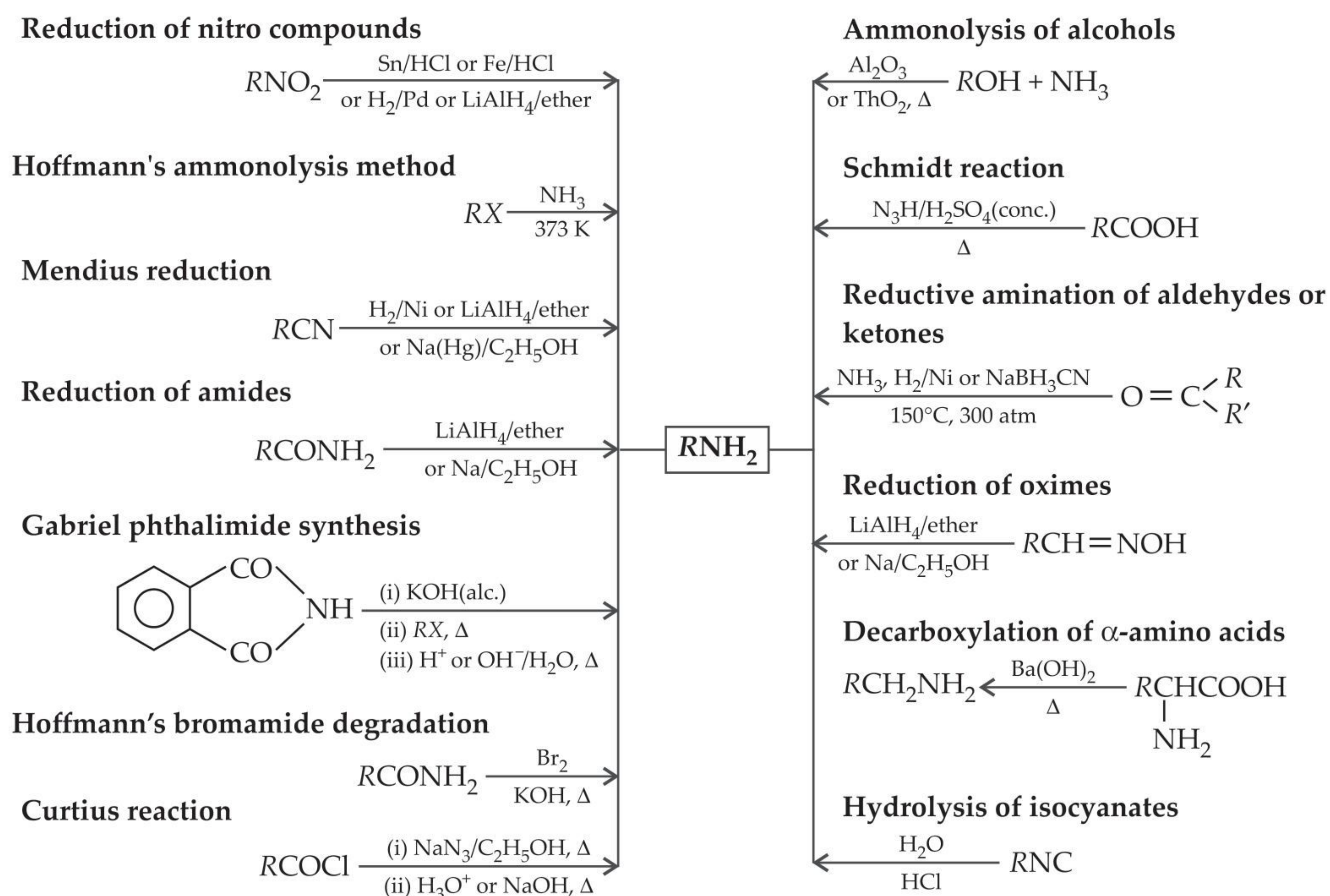
## Classification



## Structure

- ◆ Nitrogen orbitals in amines are  $sp^3$ -hybridised and the geometry of amines is pyramidal. Due to the presence of unshared pair of electrons, the angle  $C-N-E$ , (where  $E$  is  $C$  or  $H$ ) is less than  $109.5^\circ$ .

## Methods of Preparation





## Physical properties

- ◆ Lower amines are gases and liquids but higher amines are solids.
- ◆ Primary and secondary amines have higher boiling points than other organic compounds due to hydrogen bonding.
- ◆ Primary and secondary amines are soluble in water due to hydrogen bonding between  $\text{>NH}_2$  and  $\text{H}_2\text{O}$  molecules.

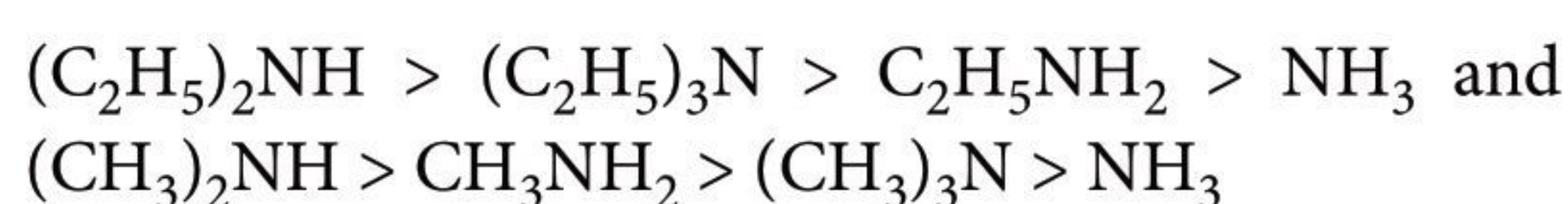
## Chemical properties

### ◆ Basic character of amines :

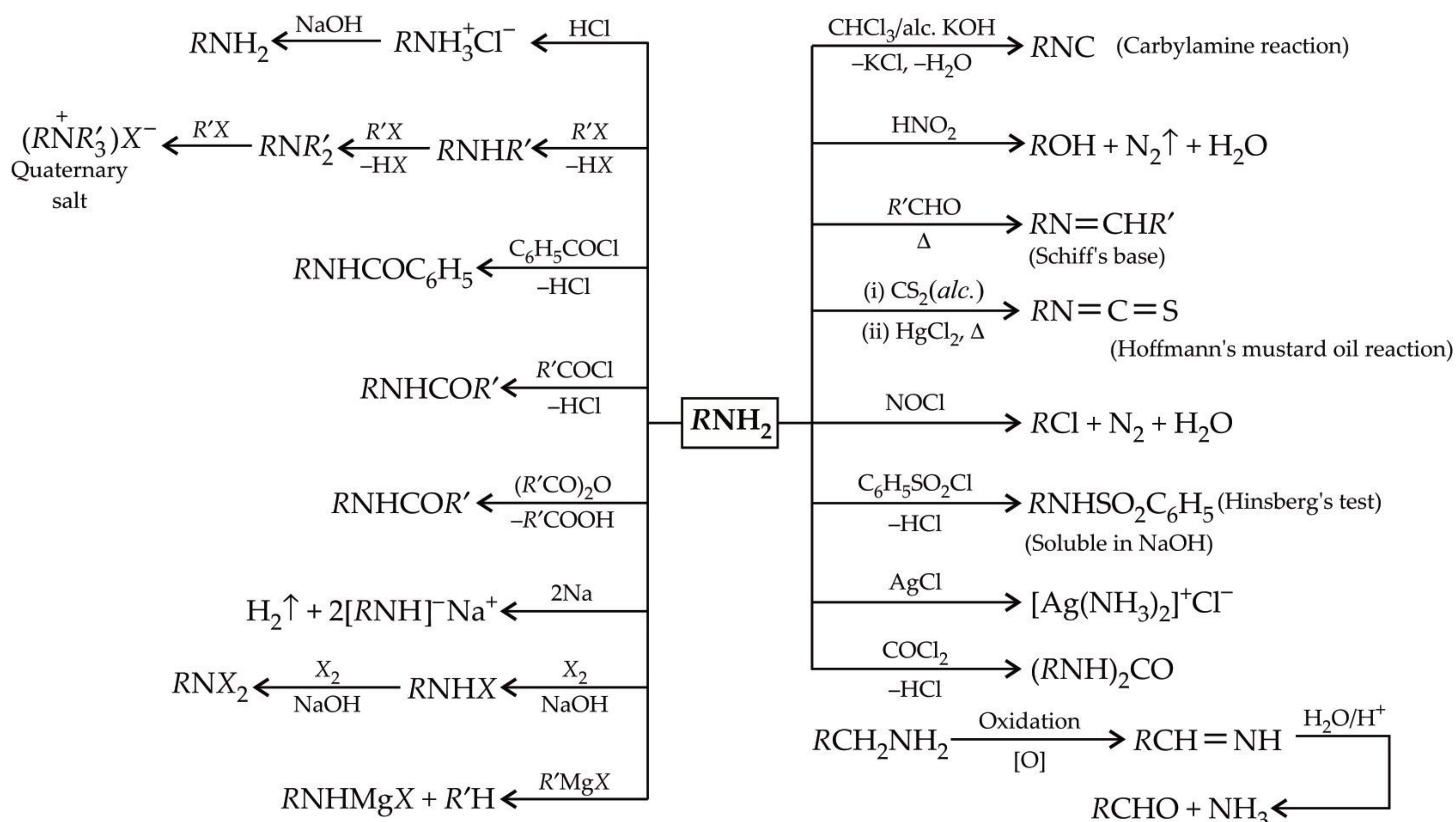
- Amines are basic in nature due to the presence of lone pair of electrons on nitrogen atom.
- Aliphatic amines are stronger bases than

ammonia due to +I effect of alkyl groups present in amines.

- Aromatic amines are weaker bases than ammonia due to -I effect of aryl group.
- Beside inductive effect, there are other effects like steric effect, solvation effect, resonance effect which affect the basic strength of amines.
- In gaseous phase, the order of basicity of amines is  $3^\circ \text{ amine} > 2^\circ \text{ amine} > 1^\circ \text{ amine} > \text{NH}_3$ .
- In aqueous phase, despite of inductive effect, solvation effect and steric hindrance also play an important role. Thus, the order of basicity of amines is



### ◆ Chemical Reactions :



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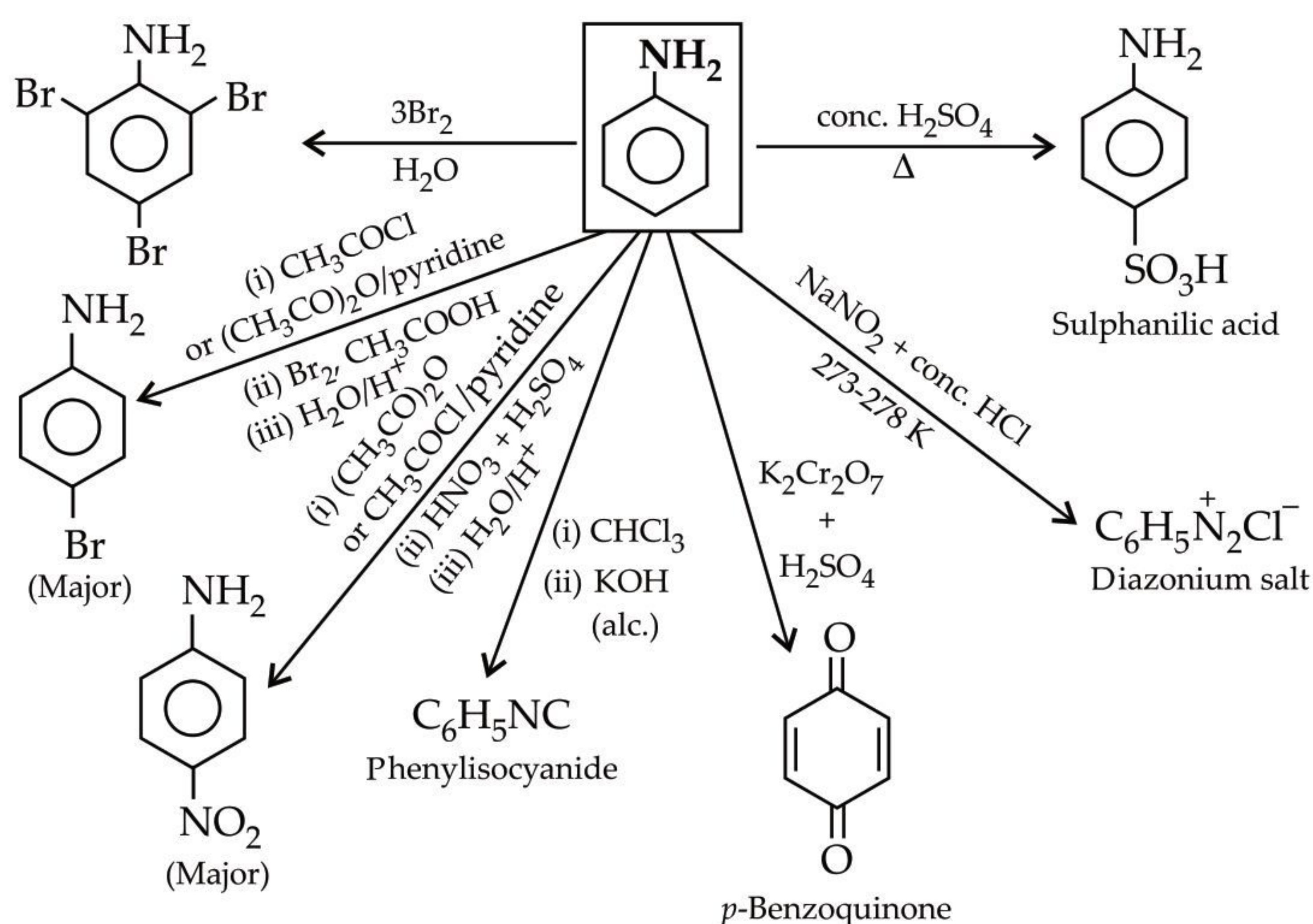
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- ◆ **Electrophilic substitution reactions of arylamines :** Aniline undergoes electrophilic substitution reactions.  $-\text{NH}_2$  group is *ortho*- and *para*-directing and a powerful activating group.



### Identification of Primary, Secondary and Tertiary Amines

	Test	Primary amine	Secondary amine	Tertiary amine
1.	Reaction with nitrous acid.	Gives alcohol with effervescence of $\text{N}_2$ gas.	Gives oily nitrosoamine which gives Liebermann's nitrosoamine test.	Forms nitrite in cold which is soluble in water and on heating gives nitrosoamine.
2.	Reaction with benzene sulphonyl chloride ( <i>Hinsberg's reagent</i> )	Gives <i>N</i> -alkylbenzene-sulphonamide which is soluble in alkali.	Gives <i>N,N</i> -dialkylbenzene sulphonamide which is insoluble in alkali.	No reaction
3.	<i>Carbylamine test</i> : Reaction with chloroform and alcoholic $\text{KOH}$	Forms carbylamine or isocyanide ( $\text{RNC}$ ) with characteristic unpleasant odour.	No reaction	No reaction
4.	<i>Hofmann's mustard oil reaction</i> : Reaction with $\text{CS}_2$ and $\text{HgCl}_2$ .	Forms <i>N</i> -substituted isothiocyanate with characteristic unpleasant smell of mustard oil.	No reaction	No reaction

### Uses

- ◆ Aliphatic amines with low molecular mass are used as solvents.
- ◆ As intermediates in drug manufacture.
- ◆ Quaternary ammonium salts of long chain aliphatic amines are used as detergents.
- ◆ Aromatic amines are used for the manufacture of polymers, dyes and as intermediates for additives in rubber industry.

### Questions for Practice

- Write IUPAC name of the following compound :  $(\text{CH}_3\text{CH}_2)_2\text{NCH}_3$  (Delhi 2017)
- How will you convert the following :

(i) Nitrobenzene into aniline

(ii) Ethanoic acid into methanamine (Delhi 2014)

- Arrange the following compounds as directed :

(i) In increasing order of solubility in water :



(ii) In increasing order of boiling point :



- Arrange the following in increasing order of base strength in gas phase.



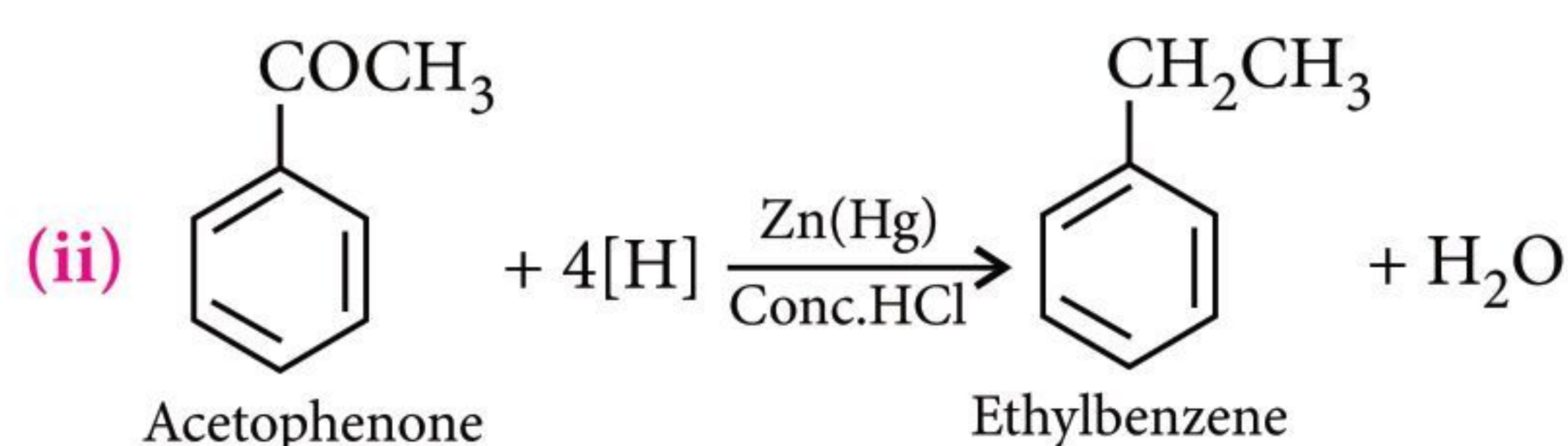
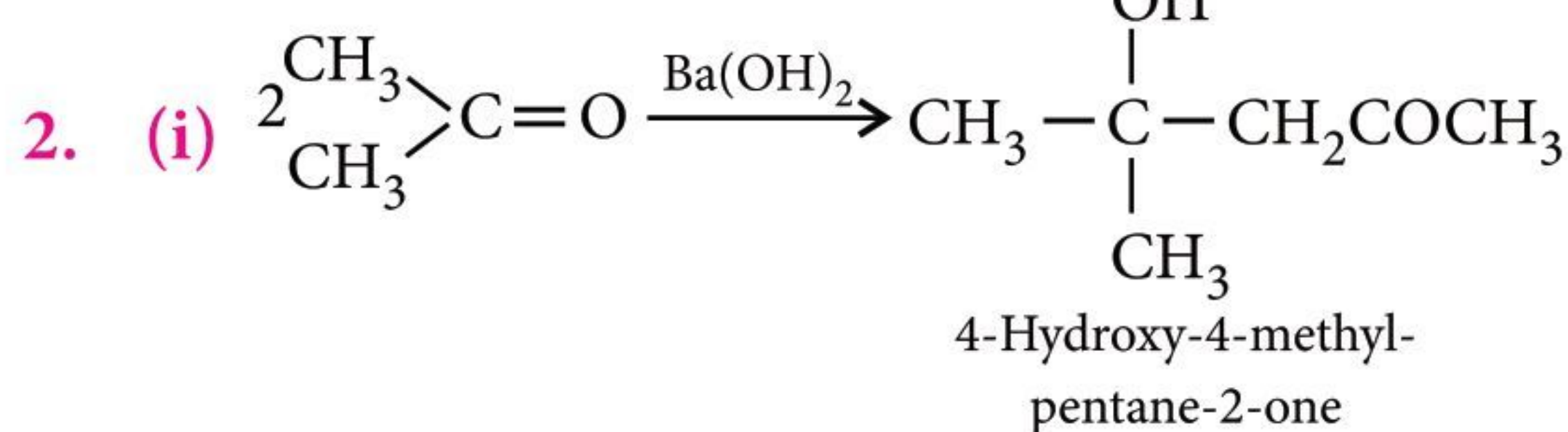
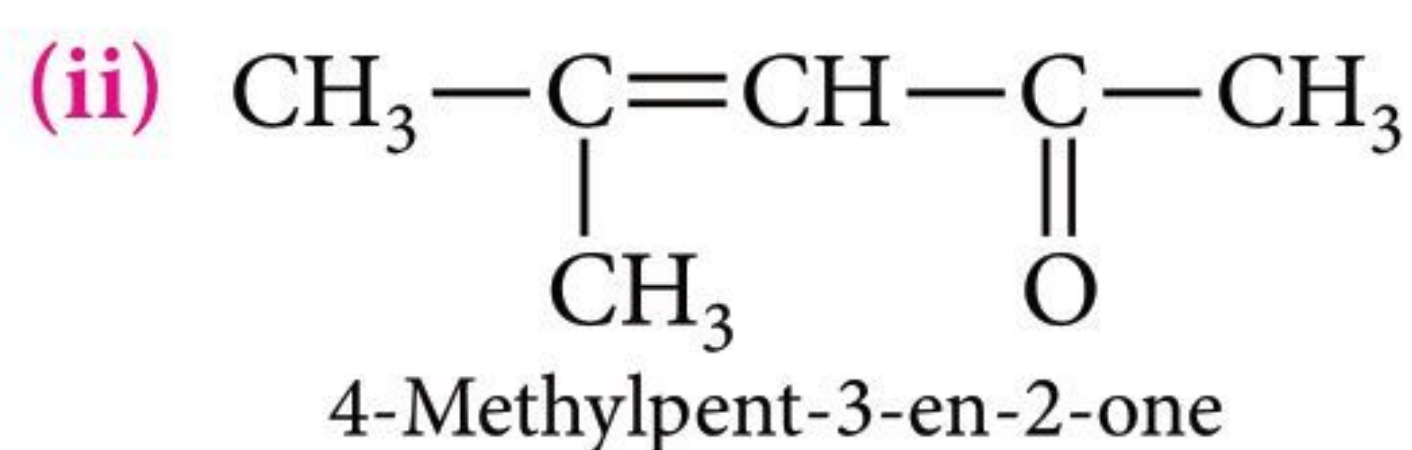
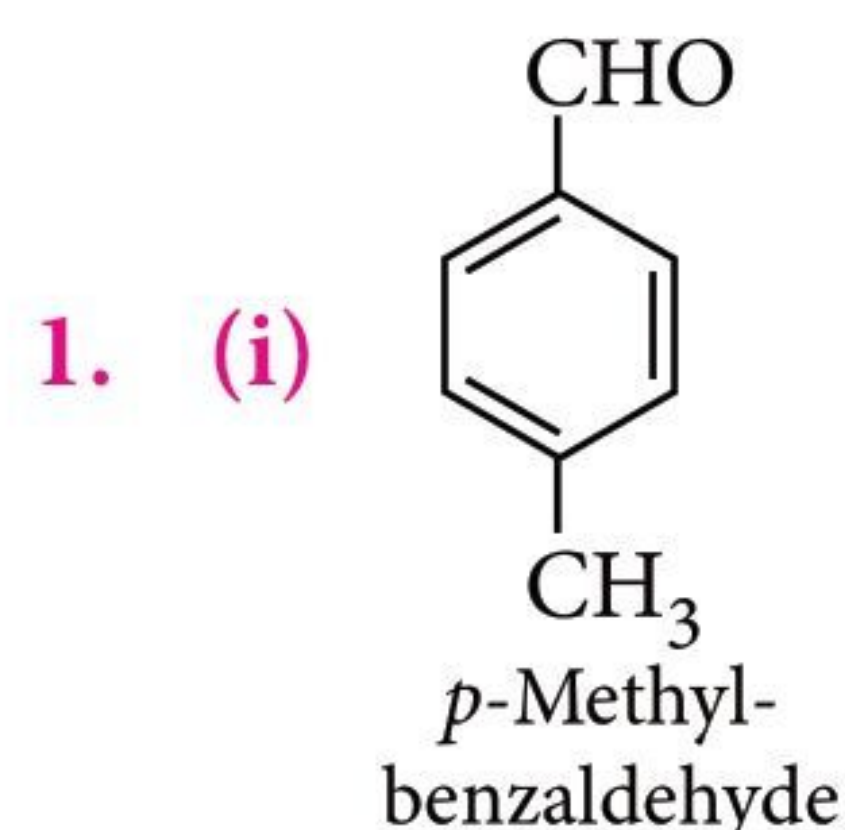
- Distinguish between the following :

(i)  $\text{CH}_3\text{CH}_2\text{NH}_2$  and  $(\text{CH}_3\text{CH}_2)_2\text{NH}$

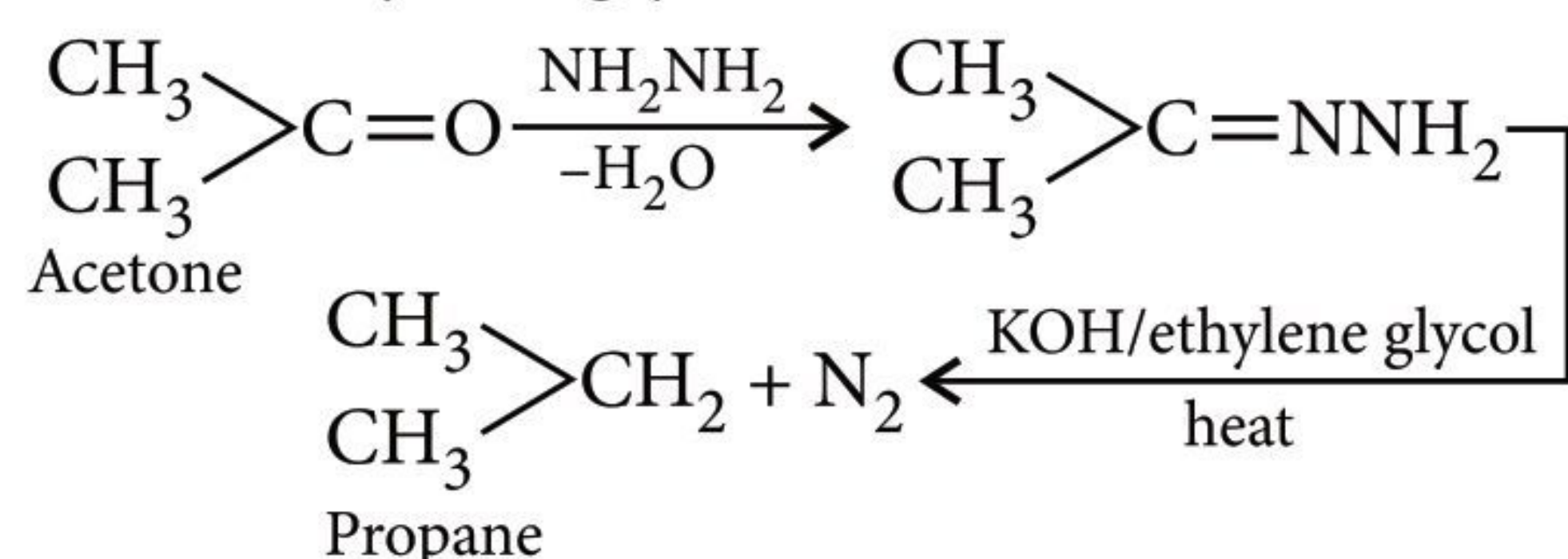
(ii) Aniline and  $\text{CH}_3\text{NH}_2$  (2020)



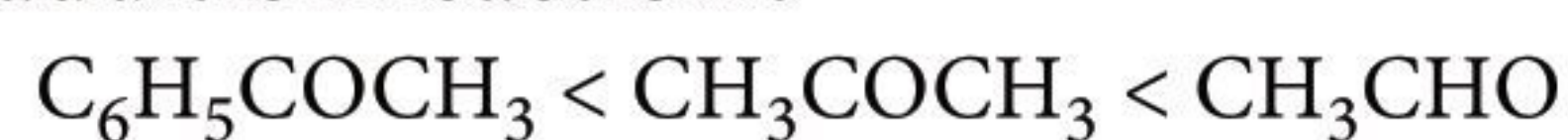
## Solutions



3. (a) **Wolff-Kishner reduction**: The carbonyl group of aldehydes and ketones is reduced to  $>\text{CH}_2$  group on treatment with hydrazine followed by heating with potassium hydroxide in a high boiling solvent such as ethylene glycol.



(b) Increasing order of reactivity towards nucleophilic addition reaction:



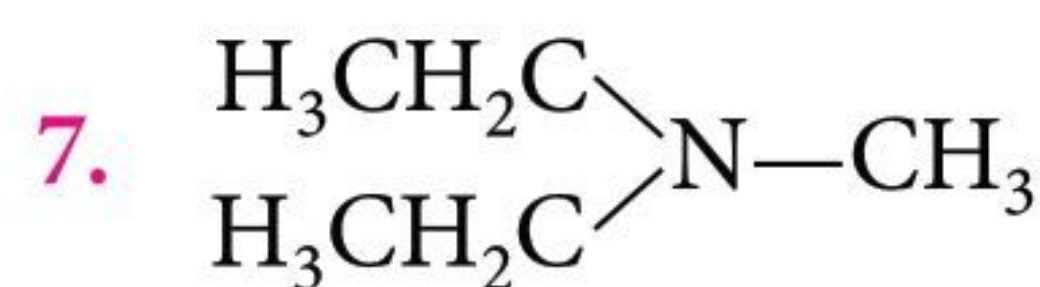
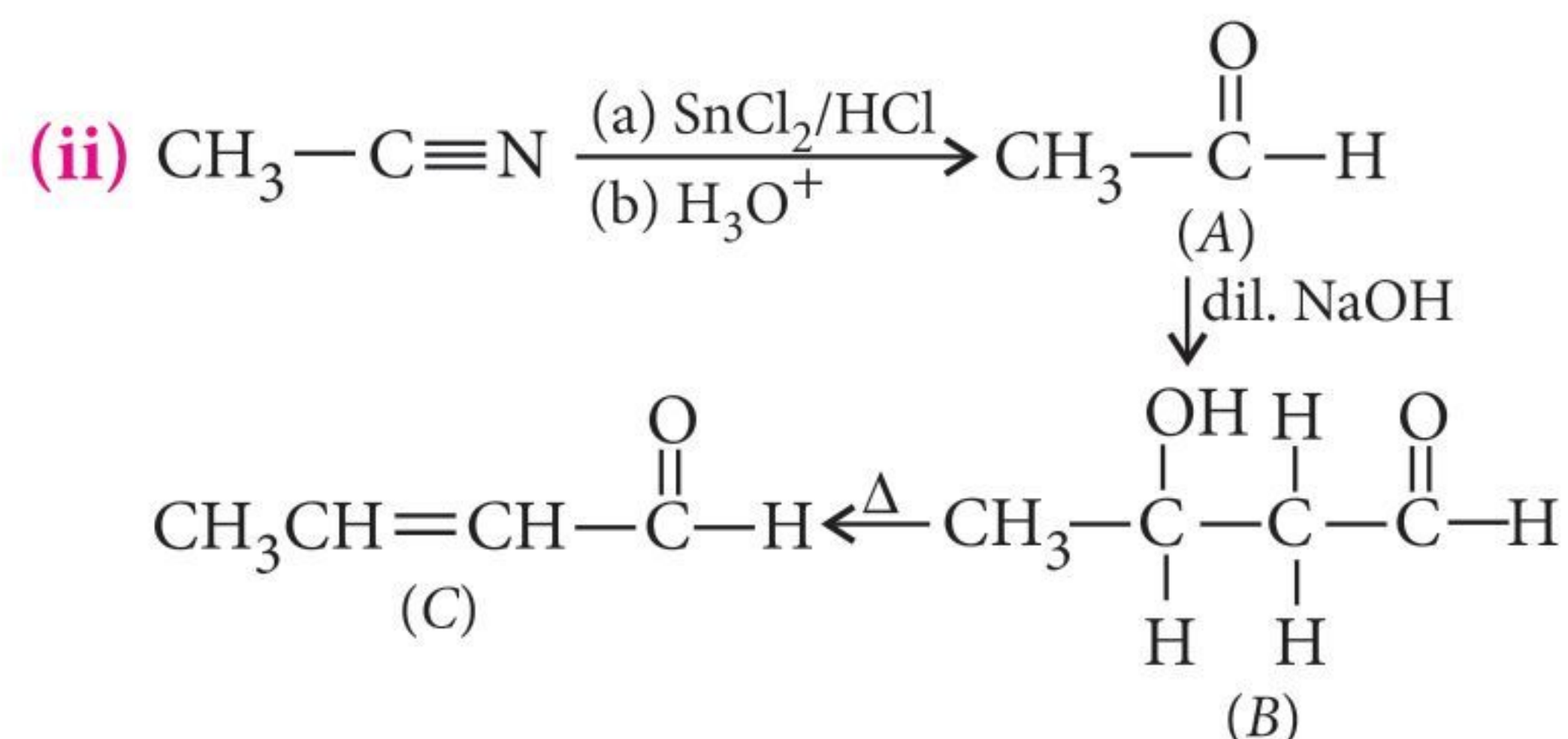
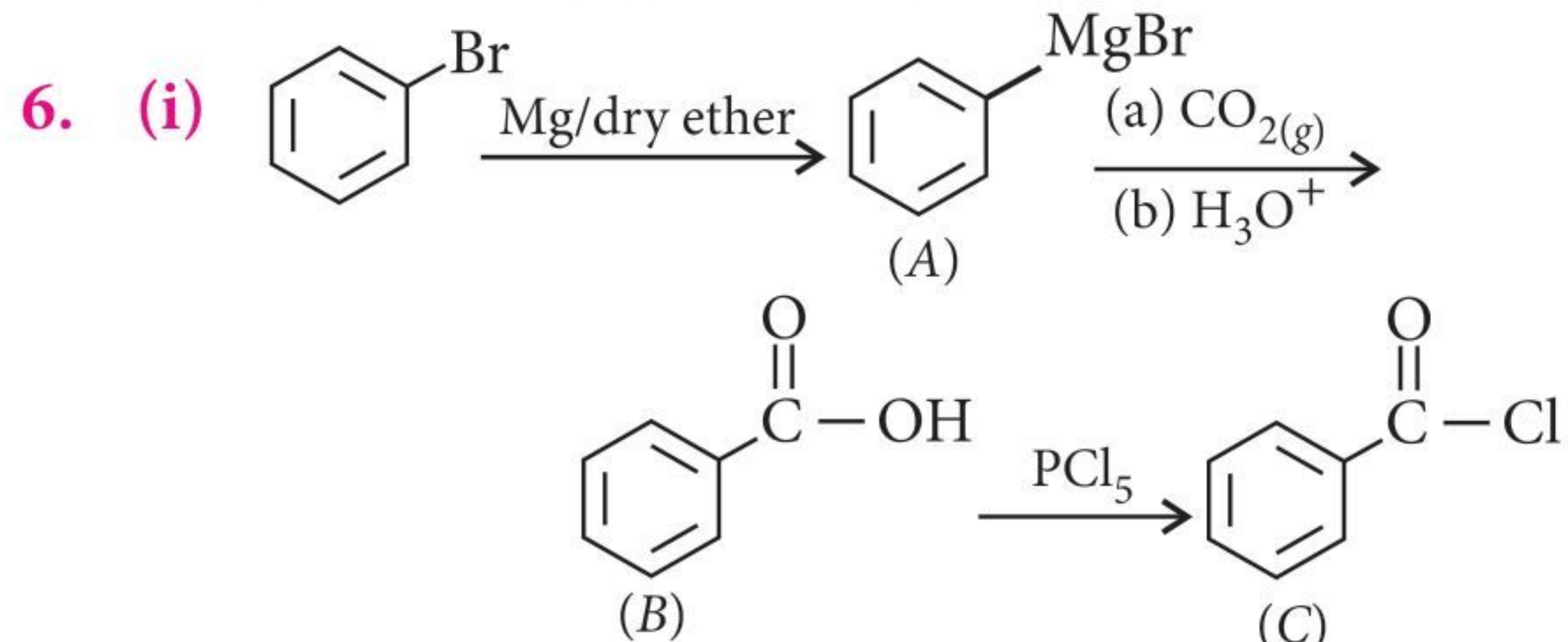
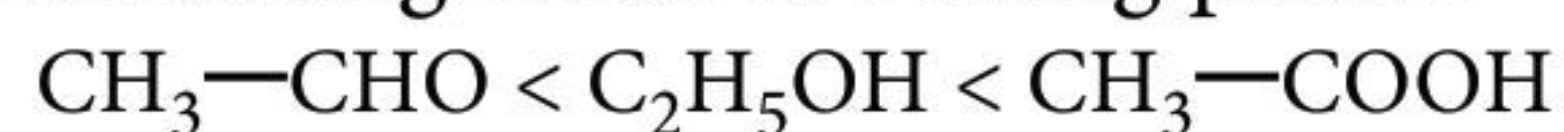
(c) Formula of compounds A and B = C<sub>3</sub>H<sub>6</sub>O. B forms yellow precipitate of iodoform. Hence, B must contain  $-\text{COCH}_3$  group. Therefore,

compound 'B' must be  $\text{CH}_3-\overset{\text{O}}{\underset{\text{||}}{\text{C}}}-\text{CH}_3$ .

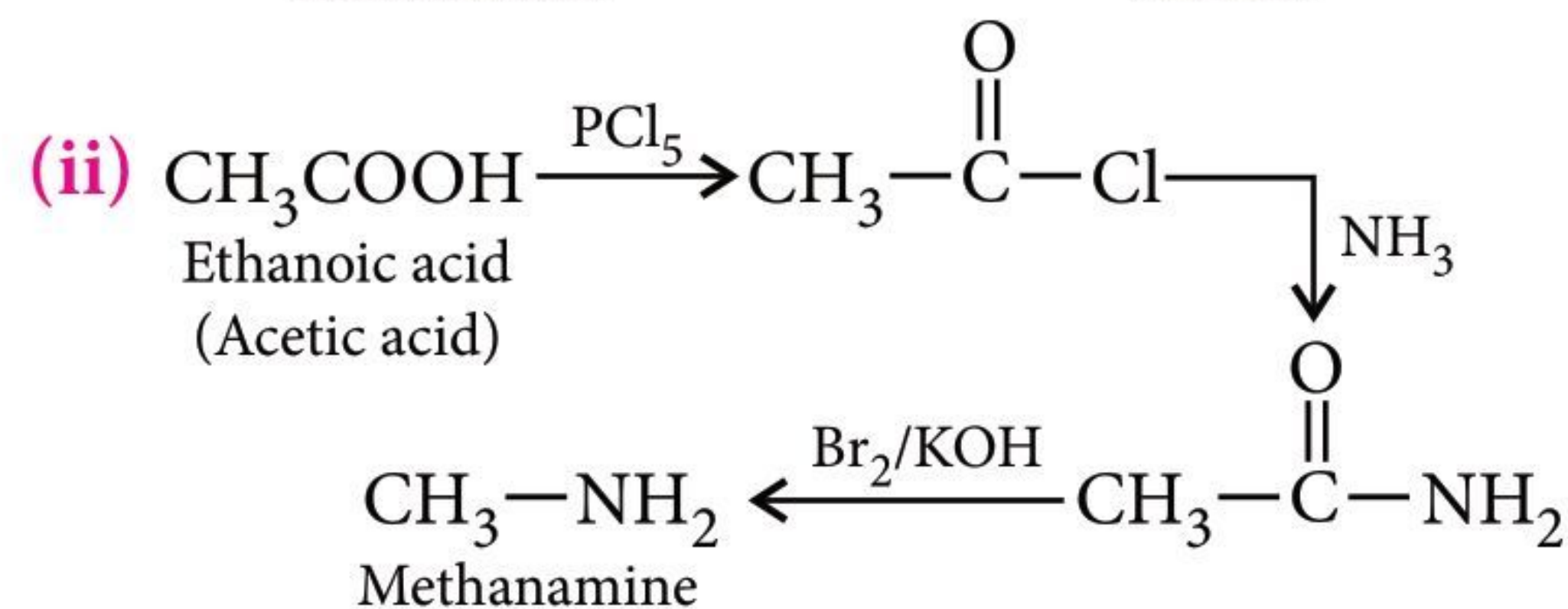
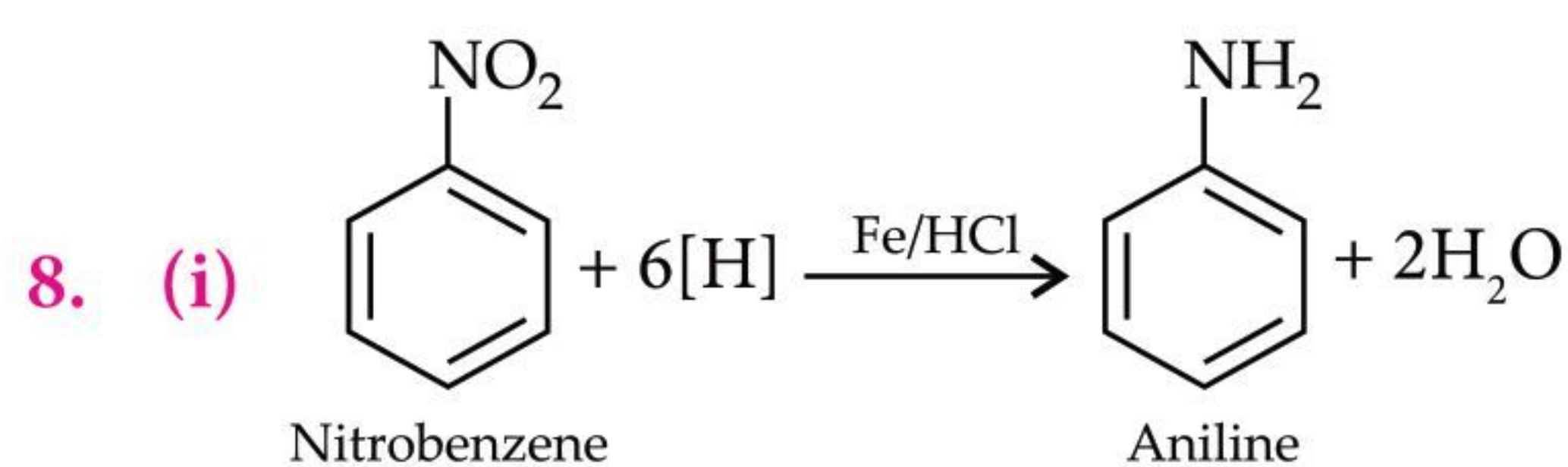
A does not give iodoform test and it is functional isomer of B thus, it may be CH<sub>3</sub>CH<sub>2</sub>CHO.

4. (a)

5. Increasing order of boiling point:



IUPAC name: N-Ethyl-N-methylethanamine



9. (i)  $\text{C}_6\text{H}_5\text{NH}_2 < (\text{CH}_3)_2\text{NH} < \text{CH}_3\text{NH}_2$

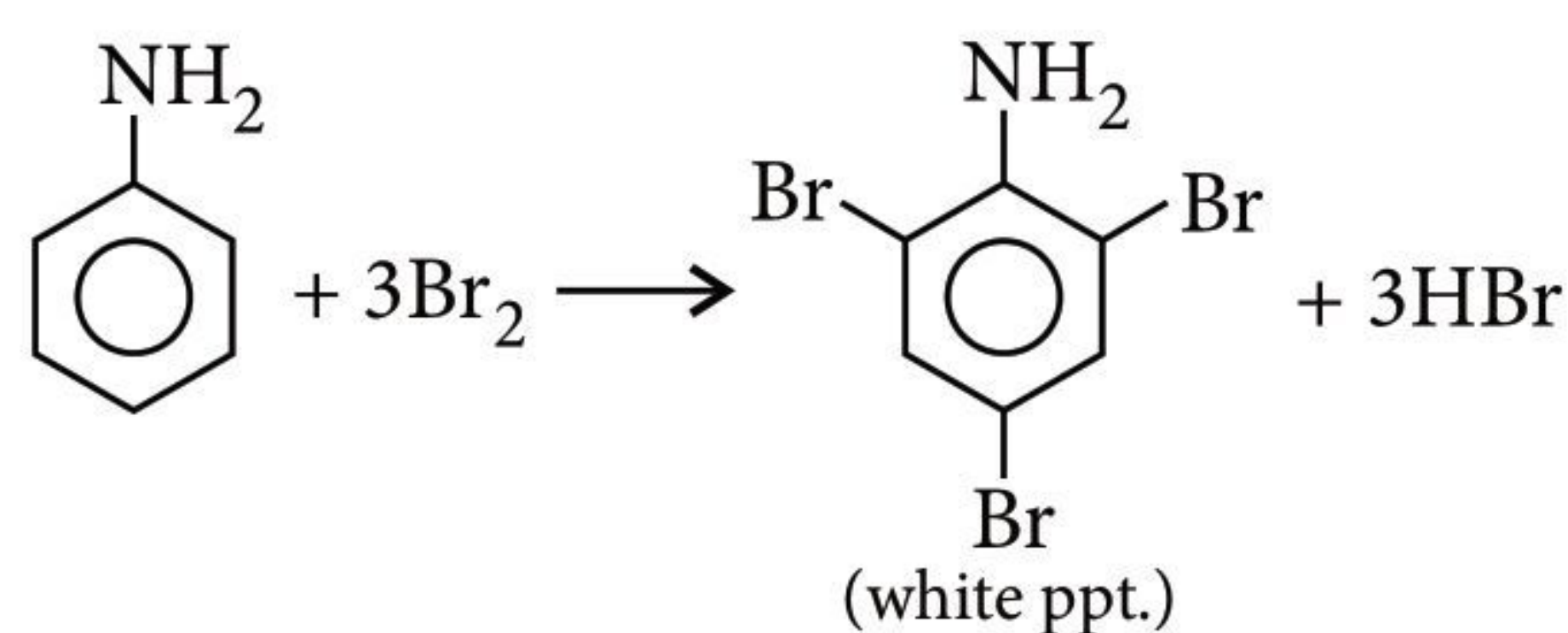
1° amines are more soluble in water than 2° amines. Aniline due to large hydrophobic benzene ring is least soluble.

(ii) 1° amines have two, 2° amines have one while 3° amines have no hydrogen linked to nitrogen. The degree of association due to hydrogen bonding and hence the boiling point increase as  $(\text{C}_2\text{H}_5)_3\text{N} < (\text{C}_2\text{H}_5)_2\text{NH} < \text{C}_2\text{H}_5\text{NH}_2$

10.  $\text{C}_2\text{H}_5\text{NH}_2 < (\text{C}_2\text{H}_5)_2\text{NH} < (\text{C}_2\text{H}_5)_3\text{N}$

11. (i) When heated with an alcoholic solution of KOH and CHCl<sub>3</sub>, ethylamine gives foul smelling ethyl isocyanide. Diethylamine does not give this test.

(ii) Aniline gives white or brown precipitate with bromine water.



Methanamine does not react with bromine water.





# CBSE

## warm-up!

Term-II

CLASS-XII

### Practice Paper 2022

Time Allowed : 2 hours  
Maximum Marks : 35

**General Instructions :** Read the following instructions carefully.

1. There are 12 questions in this question paper with internal choice.
2. SECTION A - Q. No. 1 to 3 are very short answer questions carrying 2 marks each.
3. SECTION B - Q. No. 4 to 11 are short answer questions carrying 3 marks each.
4. SECTION C - Q. No. 12 is case based question carrying 5 marks.
5. All questions are compulsory.
6. Use of log tables and calculators is not allowed.

#### SECTION - A

1. Calculate the equilibrium constant for the reaction  

$$\text{Fe}^{2+} + \text{Ce}^{4+} \rightleftharpoons \text{Fe}^{3+} + \text{Ce}^{3+}$$
 Given,  $E^\circ_{\text{Ce}^{4+}/\text{Ce}^{3+}} = 1.44 \text{ V}$ ;  $E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.68 \text{ V}$
2. The half-life period of a reaction is 140 seconds. How much of the reactant is left after 560 seconds?
3. Fluorine is more electronegative than chlorine but *p*-fluorobenzoic acid is a weaker acid than *p*-chlorobenzoic acid. Explain.

#### SECTION - B

4. Using IUPAC norm write the systematic names of the following:
  - (i)  $[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{NH}_2\text{CH}_3)]\text{Cl}$
  - (ii)  $[\text{Co}(\text{NH}_3)_4\text{Cl}(\text{NO}_2)]\text{Cl}$
  - (iii)  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$
5. A first order reaction is 20% complete in 20 minutes. How long will it take to be 75% complete?

OR

- (i) Define elementary step in a reaction.
- (ii) For the reaction,  $2\text{N}_2\text{O}_{5(g)} \rightarrow 4\text{NO}_{2(g)} + \text{O}_{2(g)}$ , the rate of formation of  $\text{NO}_{2(g)}$  is  $2.8 \times 10^{-3} \text{ M s}^{-1}$ . Calculate the rate of disappearance of  $\text{N}_2\text{O}_{5(g)}$ .

$E^\circ_{(M^{2+}/M)}$	Cr	Mn	Fe	Co	Ni	Cu
	-0.91	-1.18	-0.44	-0.28	-0.25	+0.34

From the given data of  $E^\circ$  values, answer the following questions :

- (i) Why is  $E^\circ_{(\text{Cu}^{2+}/\text{Cu})}$  value exceptionally positive?
- (ii) Why is  $E^\circ_{(\text{Mn}^{2+}/\text{Mn})}$  value highly negative as compared to other elements?
- (iii) Which is a stronger reducing agent  $\text{Cr}^{2+}$  or  $\text{Fe}^{2+}$ ? Given that :  
 $E^\circ_{\text{Cr}^{3+}/\text{Cr}^{2+}} = -0.41 \text{ V}$ ;  $E^\circ_{\text{Fe}^{2+}/\text{Fe}^{3+}} = -0.77 \text{ V}$

OR

Account for the following :

- (i) The transition metals and their compounds act as good catalysts.



(ii) The oxides with lowest oxidation state of transition metal is basic, the highest is amphoteric/acidic.

(iii) A transition metal exhibits higher oxidation states in oxides and fluorides.

7. How are colloids classified on the basis of

(i) physical states of components and

(ii) interaction between dispersed phase and dispersion medium?

OR

Explain how the two types of processes of adsorption (physisorption and chemisorption) are influenced by the prevailing temperature, the surface area of adsorbent and the activation energy of the process?

8. An aromatic compound 'A' on treatment with aqueous ammonia and heating, forms compound 'B' which on heating with  $\text{Br}_2$  and KOH forms a compound 'C' of molecular formula  $\text{C}_6\text{H}_7\text{N}$ . Write the structures and IUPAC names of compounds A, B and C.

9. (i) Define Kohlrausch's law of independent migration of ions.

(ii) Calculate the degree of dissociation ( $\alpha$ ) of acetic acid if its molar conductivity ( $\Lambda_m$ ) is  $39.05 \text{ S cm}^2 \text{ mol}^{-1}$ .

(Given :  $\lambda_{(\text{H}^+)}^\circ = 349.68 \text{ S cm}^2 \text{ mol}^{-1}$  and  $\lambda_{(\text{CH}_3\text{COO}^-)}^\circ = 40.9 \text{ S cm}^2 \text{ mol}^{-1}$ )

10. (i) What is the difference between a complex and a double salt?

(ii) Account for the following:

$\text{Ni}(\text{CO})_4$  possesses tetrahedral geometry while  $[\text{Ni}(\text{CN})_4]^{2-}$  is square planar.

11. Arrange the following :

(i) In decreasing order of the  $\text{p}K_b$  values:  $\text{C}_2\text{H}_5\text{NH}_2$ ,  $\text{C}_6\text{H}_5\text{NHCH}_3$ ,  $(\text{C}_2\text{H}_5)_2\text{NH}$  and  $\text{C}_6\text{H}_5\text{NH}_2$

(ii) Increasing order of boiling point :  $\text{C}_2\text{H}_5\text{OH}$ ,  $(\text{CH}_3)_2\text{NH}$ ,  $\text{C}_2\text{H}_5\text{NH}_2$

(iii) Increasing order of solubility in water :  $\text{C}_6\text{H}_5\text{NH}_2$ ,  $(\text{C}_2\text{H}_5)_2\text{NH}$ ,  $\text{C}_2\text{H}_5\text{NH}_2$

OR

(i) Give a chemical test to distinguish between aniline and *N*-methylaniline.

(ii) How will you convert *p*-toluidine into 2-bromo-4-methylaniline

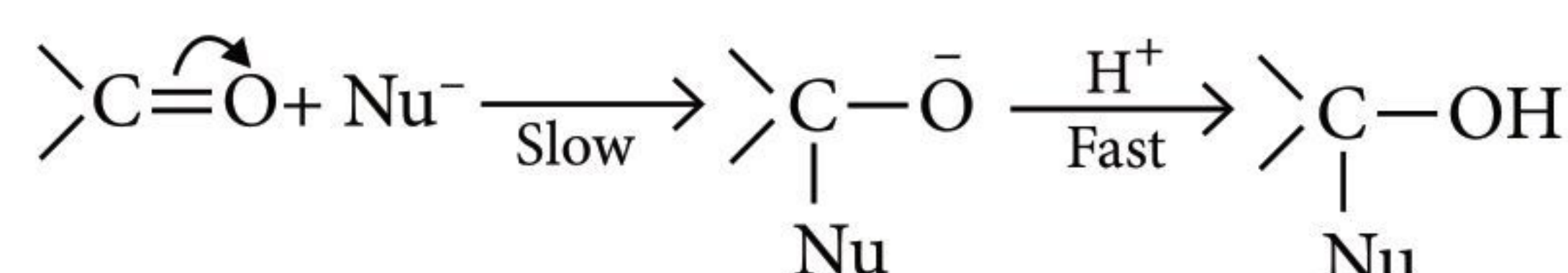
## SECTION - C

12. Read the passage given below and answer the questions that follow:

The carbonyl group is highly polar due to shifting of the  $\pi$ -electrons towards the more electronegative oxygen atom.



The two charged centres can be attacked by nucleophile (at carbon) and electrophile (at oxygen). In addition reactions, nucleophilic attack is preferred because the anion produced is more stable than the cation.



The order of reactivity for aldehydes and ketones towards nucleophilic addition is:

$\text{HCHO} > \text{CH}_3\text{CHO} > \text{C}_2\text{H}_5\text{CHO} > \text{C}_3\text{H}_7\text{CHO} \dots$

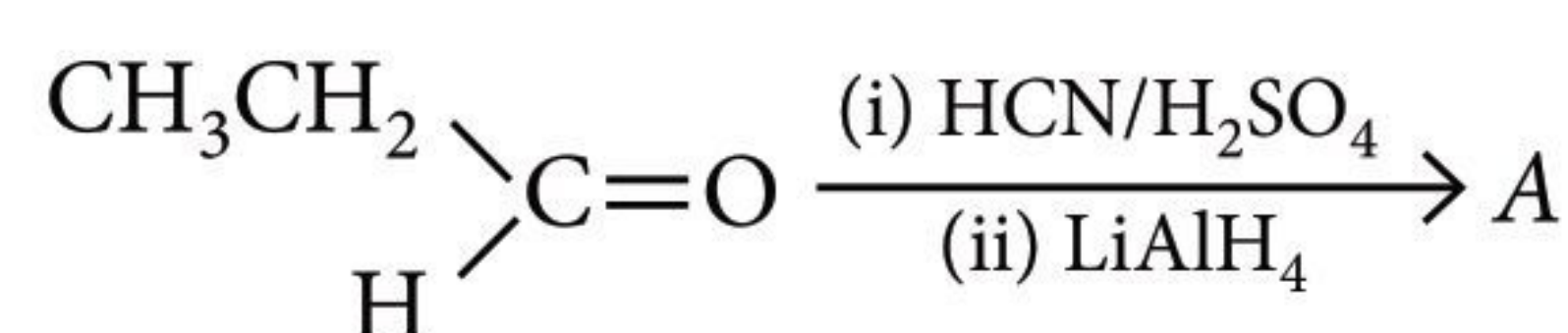
$\text{HCHO} > \text{CH}_3\text{CHO} > \text{CH}_3\text{COCH}_3 > \text{CH}_3\text{COC}_2\text{H}_5 > \text{C}_2\text{H}_5\text{COC}_2\text{H}_5 \dots$

As the size of alkyl group increases, its +I effect decreases the positive charge on the carbonyl carbon and thus decreases its reactivity.

(a) What is meant by aldol? Give an example.

(b) The double bond in carbonyl compounds is reactive towards nucleophilic reagents, e.g.  $\text{CN}^-$ ; whereas in alkenes, it is not. Why?

(c) Complete the following reaction with appropriate structure:



(d) Account for the following :

(i)  $\text{CH}_3\text{CHO}$  is more reactive than  $\text{CH}_3\text{COCH}_3$  towards reaction with HCN.

(ii) There are two  $-\text{NH}_2$  groups in semicarbazide ( $\text{H}_2\text{NNHCONH}_2$ ), however, only one is involved in the formation of semicarbazone.

OR

Draw structures of the following derivatives.

(i) The 2, 4-dinitrophenylhydrazone of benzaldehyde

(ii) The ethylene ketal of hexan-3-one



## SOLUTIONS

1. Applying,  $E_{\text{cell}}^{\circ} = \frac{0.0591}{n} \log K_c$

$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = 1.44 - 0.68 = 0.76 \text{ V}$$

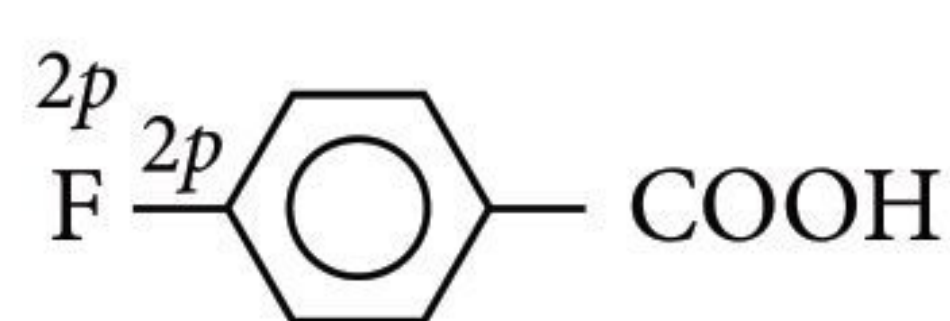
Thus,  $0.76 = \frac{0.0591}{1} \log K_c$  ;  $\log K_c = 12.86$

Taking antilog,  $K_c = 7.2 \times 10^{12}$

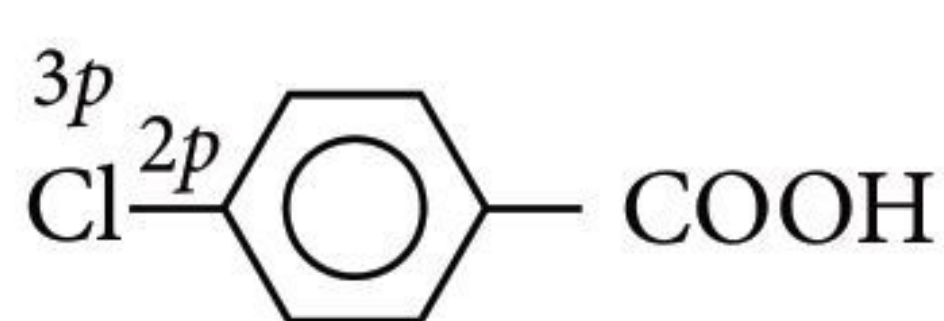
2. Number of half-lives  $= \frac{560}{140} = 4$

Amount left after 4 half-lives  $= \frac{1}{2^4} = \frac{1}{16}$  of initial concentration.

3. Halogens are more electronegative than carbon and also possess lone pairs of electrons. Therefore, halogens can exert  $-I$  and  $+R$  effects. In F atom, the lone pairs of electrons are present in  $2p$ -orbitals but in Cl atom, they are present in  $3p$ -orbitals. Since  $2p$ -orbitals of F and C are of almost same size, therefore,  $+R$  effect is more pronounced in  $p$ -fluorobenzoic acid than in  $p$ -chlorobenzoic acid.



Stronger  $+R$  effect



Weaker  $+R$  effect.

Thus, in  $p$ -fluorobenzoic acid,  $+R$  effect outweighs the  $-I$  effect and therefore, it is weaker acid than  $p$ -chlorobenzoic acid (having more  $-I$  effect than  $+R$  effect).

4. (i) Diamminechloridomethylamineplatinum(II) chloride

(ii) Tetraamminechloridonitrito-N-cobalt(III) chloride

(iii) Hexaaquamanganese(II) ion

5.  $k = \frac{2.303}{t} \log \frac{a}{(a-x)}$

$t_{20\%} = 20 \text{ minutes} = \frac{2.303}{k} \log \frac{100}{(100-20)}$  ... (i)

$t_{75\%} = \frac{2.303}{k} \log \frac{100}{(100-75)}$  ... (ii)

Divide eqn. (ii) by eqn. (i)

$$\frac{t_{75\%}}{20} = \frac{\log 4}{\log \frac{5}{4}} = \frac{0.6021}{0.0969}$$

$$t_{75\%} = \frac{20 \times 0.6021}{0.0969} = 124.27 \text{ minutes}$$

OR

(i) Elementary step : Each step of a complex reaction is called an elementary step.

(ii) Given,  $\frac{d[\text{NO}_2]}{dt} = 2.8 \times 10^{-3} \text{ M s}^{-1}$

According to rate law expression,

$$-\frac{1}{2} \frac{d[\text{N}_2\text{O}_5]}{dt} = \frac{1}{4} \frac{d[\text{NO}_2]}{dt} = \frac{d[\text{O}_2]}{dt}$$

$$\therefore -\frac{1}{2} \frac{d[\text{N}_2\text{O}_5]}{dt} = \frac{1}{4} \times 2.8 \times 10^{-3}$$

$$\frac{-d[\text{N}_2\text{O}_5]}{dt} = \frac{1}{2} \times 2.8 \times 10^{-3} = 1.4 \times 10^{-3} \text{ M s}^{-1}$$

6. (i) Electrode potential ( $E^{\circ}$ ) value is the sum of three factors :

(a) Enthalpy of atomisation  $\Delta_a H$  for  $\text{Cu}_{(s)} \rightarrow \text{Cu}_{(g)}$

(b) Ionisation enthalpy  $\Delta_i H$  for  $\text{Cu}_{(g)} \rightarrow \text{Cu}_{(g)}^{2+}$

(c) Hydration enthalpy  $\Delta_{hyd} H$  for  $\text{Cu}_{(g)}^{2+} \rightarrow \text{Cu}_{(aq)}^{2+}$

In case of copper the sum of enthalpy of atomisation and ionisation enthalpy is greater than enthalpy of hydration.

This is why  $E^{\circ}_{\text{M}^{2+}/\text{M}}$  for Cu is positive.

(ii)  $\text{Mn}^{2+}$  ion has stable half-filled ( $3d^5$ ) electronic configuration. Its ionisation enthalpy value is higher in comparison to hydration enthalpy. Hence,  $E^{\circ}_{\text{Mn}^{2+}/\text{Mn}}$  is more negative.

(iii)  $\text{Cr}^{2+}$  is a stronger reducing agent than  $\text{Fe}^{2+}$ .

$E^{\circ}_{\text{Cr}^{3+}/\text{Cr}^{2+}}$  is negative ( $-0.41 \text{ V}$ ) whereas  $E^{\circ}_{\text{Fe}^{3+}/\text{Fe}^{2+}}$  is positive ( $+0.77 \text{ V}$ ). Thus  $\text{Cr}^{2+}$  is easily oxidized to  $\text{Cr}^{3+}$  but  $\text{Fe}^{2+}$  cannot be easily oxidized to  $\text{Fe}^{3+}$ . Hence,  $\text{Cr}^{2+}$  is stronger reducing agent than  $\text{Fe}^{2+}$ .

OR

(i) The transition metals and their compounds, are known for their catalytic activity. This activity is ascribed to their ability to adopt multiple oxidation states, to adsorb the reactant(s) and to form complexes. Vanadium (V) oxide (in Contact Process), finely divided iron (in Haber's Process), and nickel (in catalytic hydrogenation) are some of the examples. Catalysis involves the formation of bonds between reactant molecules and atoms at the surface of the catalyst.

(ii) Lowest oxidation compounds of transition metals are basic due to their ability to get oxidised to higher oxidation states. Whereas, the higher oxidation state of metal and compounds gets reduced to lower ones and hence acts as acidic in nature.

e.g.,  $\text{MnO}$  is basic whereas  $\text{Mn}_2\text{O}_7$  is acidic.

(iii) Transition metals of  $3d$ -series can form  $p\pi-d\pi$  bond with oxygen by utilising  $2p$ -orbital of oxygen and  $3d$ -orbital of manganese due to which they can show highest oxidation state of  $+7$ . While fluorine



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cannot form such  $p\pi - d\pi$  bond but due to its high electronegative, transition metal exhibit high oxidation state with fluorine also.

7. (i) Colloids can be classified into eight types depending upon the physical state of the dispersed phase and the dispersion medium.

Dispersed phase	Dispersion medium	Types of colloid	Examples
Solid	Solid	Solid sol	Coloured glasses, gem stones
Solid	Liquid	Sol	Paints, cell fluid
Solid	Gas	Aerosol	Smoke, dust
Liquid	Solid	Gel	Cheese, butter, jellies
Liquid	Liquid	Emulsion	Milk, hair cream
Liquid	Gas	Aerosol	Fog, mist, cloud
Gas	Solid	Solid sol	Pumice stone, foam rubber
Gas	Liquid	Foam	Froth, whipped cream

(ii) There are two types of colloidal sols:

(a) Lyophilic sols : The word lyophilic means solvent loving. They are obtained by directly mixing the dispersed phase and the dispersion medium, *e.g.*, sols of gum, gelatin, starch, etc. They are solvent attracting hence quite stable and cannot be coagulated easily.

(b) Lyophobic sols : They cannot be prepared by directly mixing the dispersed phase and dispersion medium but are prepared by special methods, *e.g.*, sols of metals. They are solvent repelling. Hydrophobic sols are easily coagulated due to repulsion between water and dispersed phase.

OR

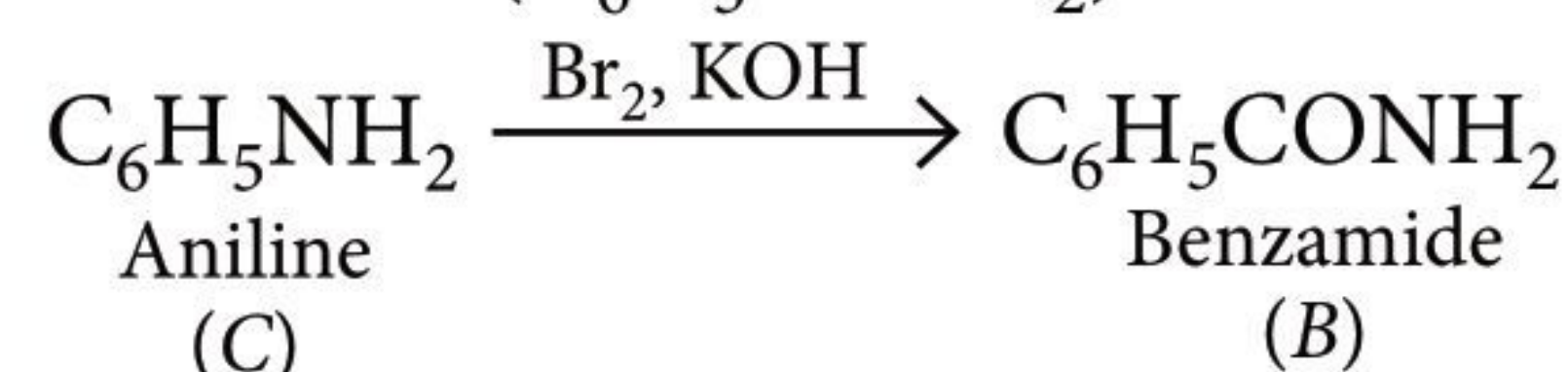
Effect of temperature : Physisorption decreases with increase of temperature and chemisorption first increases then decreases with increase of temperature.

Surface area : Greater the surface area, greater is the physisorption and chemisorption.

Activation energy : In physisorption, no appreciable activation energy is needed. In chemisorption, sometimes high activation energy is needed.

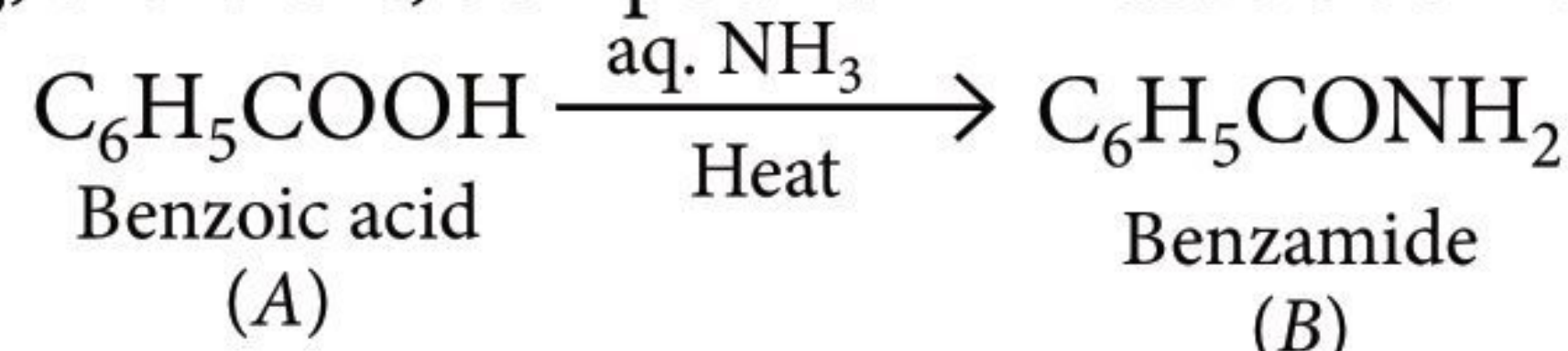
8. Since the compound C of molecular formula  $C_6H_7N$  is formed from B on treatment with  $Br_2$  and KOH (Hoffmann bromamide reaction), therefore, the compound 'B' must be an amide and 'C' must be an amine. The only aromatic amine having molecular formula  $C_6H_7N$  is  $C_6H_5NH_2$  (aniline).

Since 'C' is aniline, the amide from which is formed by must be benzamide ( $C_6H_5CONH_2$ ).



Thus, B is benzamide.

Since B is formed from A with aqueous ammonia and heating, therefore, compound 'A' must be benzoic acid.



Thus,  $A = C_6H_5COOH$ ,  $B = C_6H_5CONH_2$ ,  $C = C_6H_5NH_2$ .

9. (i) Kohlrausch's law of independent migration of ions : It states that limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte.

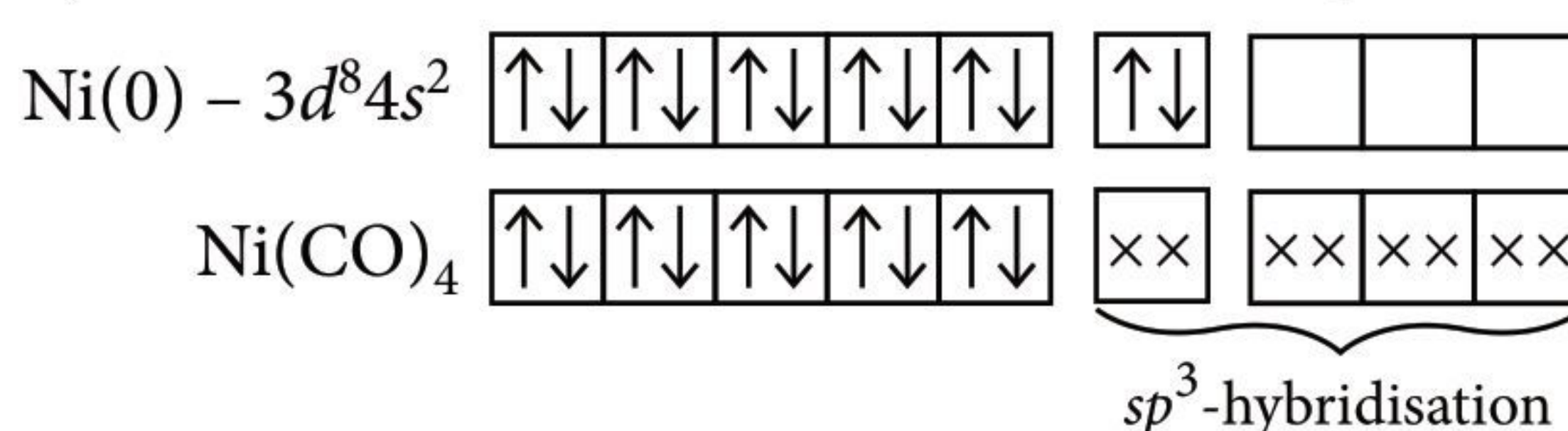
If  $\lambda_{Na^+}^\circ$  and  $\lambda_{Cl^-}^\circ$  are limiting molar conductivities of the sodium and chloride ions respectively then the limiting molar conductivity for sodium chloride is given by  $\Lambda_{m(NaCl)}^\circ = \lambda_{Na^+}^\circ + \lambda_{Cl^-}^\circ$

$$(ii) \text{ Degree of dissociation } (\alpha) = \frac{\Lambda_m}{\Lambda_m^\circ}$$

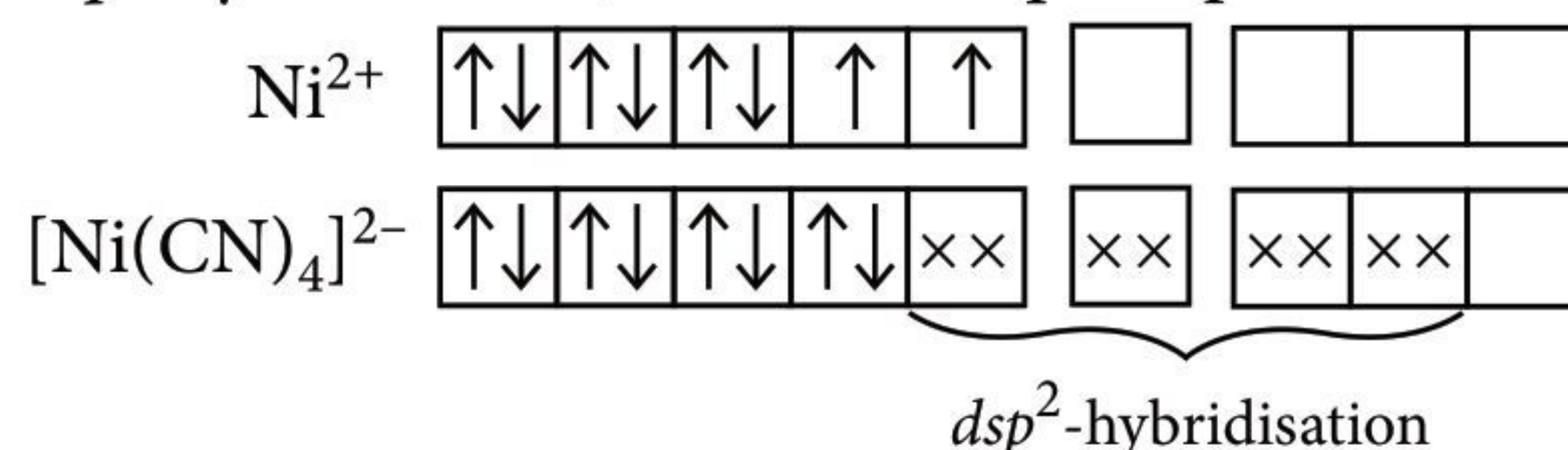
$$\alpha = \frac{39.05 \text{ S cm}^2 \text{ mol}^{-1}}{(349.68 + 40.9) \text{ S cm}^2 \text{ mol}^{-1}} = 0.1$$

10. (i) Double salts dissociate into ions completely when dissolved in water. On the other hand, in complexes, the complex ion does not dissociate.

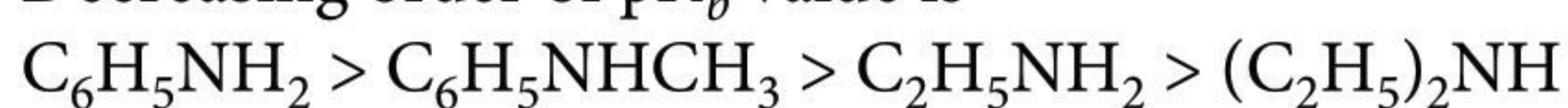
(ii) In the formation of  $Ni(CO)_4$ , nickel undergoes  $sp^3$  hybridisation, hence it is tetrahedral in shape.



In the formation of  $[Ni(CN)_4]^{2-}$ ,  $Ni^{2+}$  ion undergoes  $dsp^2$  hybridisation, hence it is square planar in shape.



11. (i) Stronger the base, lesser is the  $pK_b$  value. Decreasing order of  $pK_b$  value is

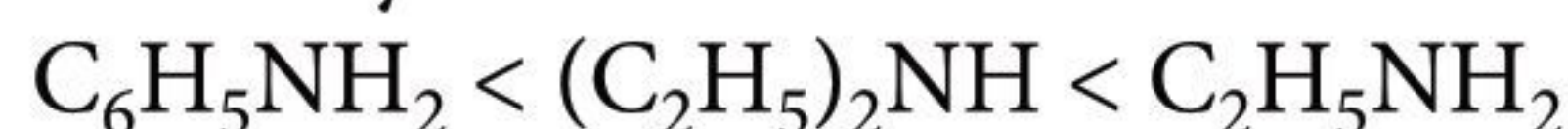


(ii) Since the electronegativity of O is more than that of N, alcohols form stronger hydrogen bonds than



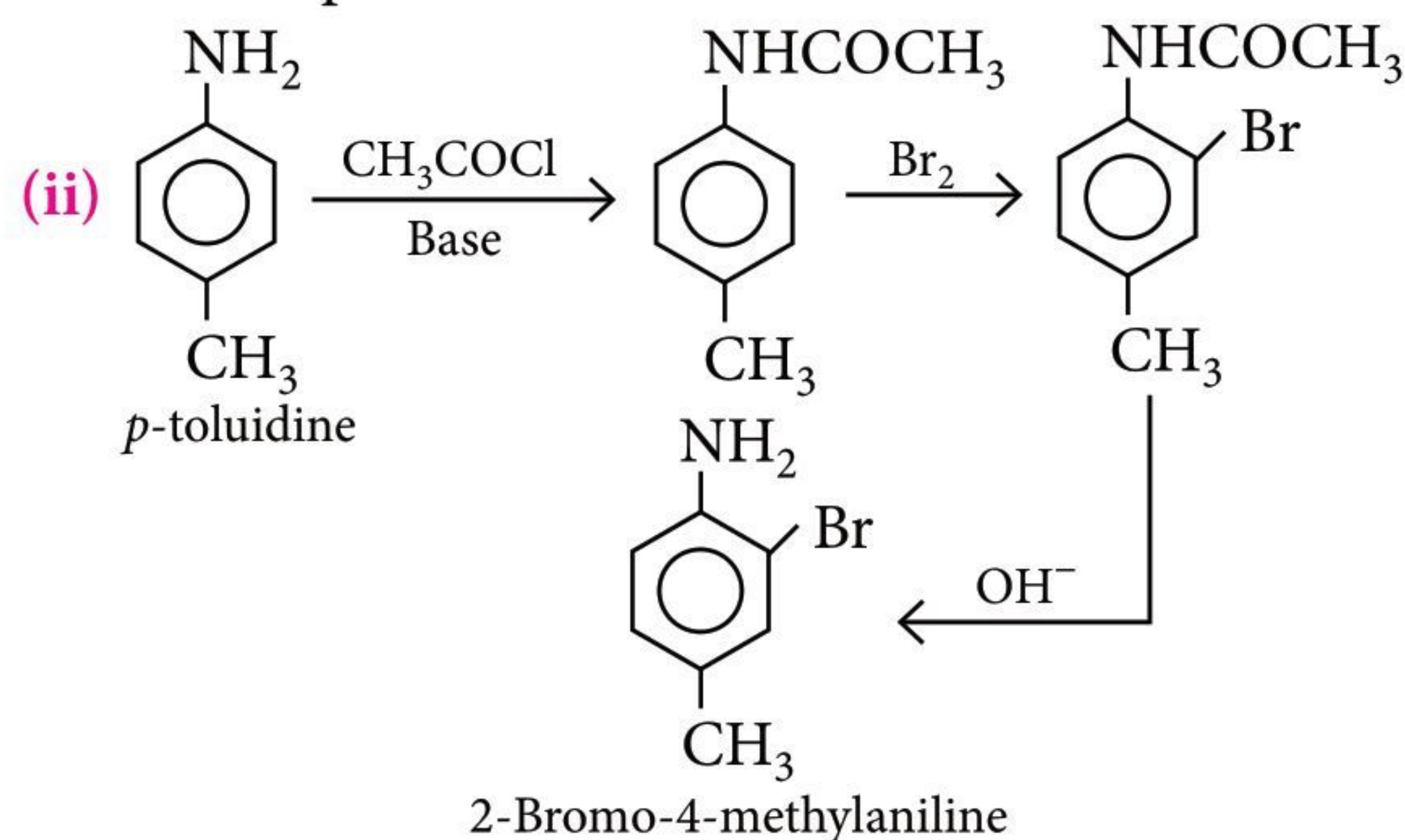
amine. Therefore, the b.pt. of  $C_2H_5OH$  (mol. mass = 46) is higher than those of  $(CH_3)_2NH$  and  $C_2H_5NH_2$  (each having mol mass = 45). Further, since the extent of hydrogen bonding depends upon the number of H-atoms on N atom, therefore,  $1^\circ$  amines with two H atoms on the N atom have higher b.pt. than  $2^\circ$  amines (of comparable molecular mass) having only one H atom on N. Thus, the boiling point of  $C_2H_5NH_2$  is more than that of  $(CH_3)_2NH$ . Thus, the b.pt. of given compounds increase as :  $(CH_3)_2NH < C_2H_5NH_2 < C_2H_5OH$

(iii) Solubility decreases with increase in molecular mass of amines due to increases in size of the hydrophobic hydrocarbon part and with the decreases in the number of H atoms on the N-atom which form hydrogen bonds. Among the given compounds,  $C_6H_5NH_2$  has higher molecular mass (93) followed by  $(C_2H_5)_2NH$  (73) while  $C_2H_5NH_2$  has lowest molecular mass of 45. Thus, the solubility increases in the order :

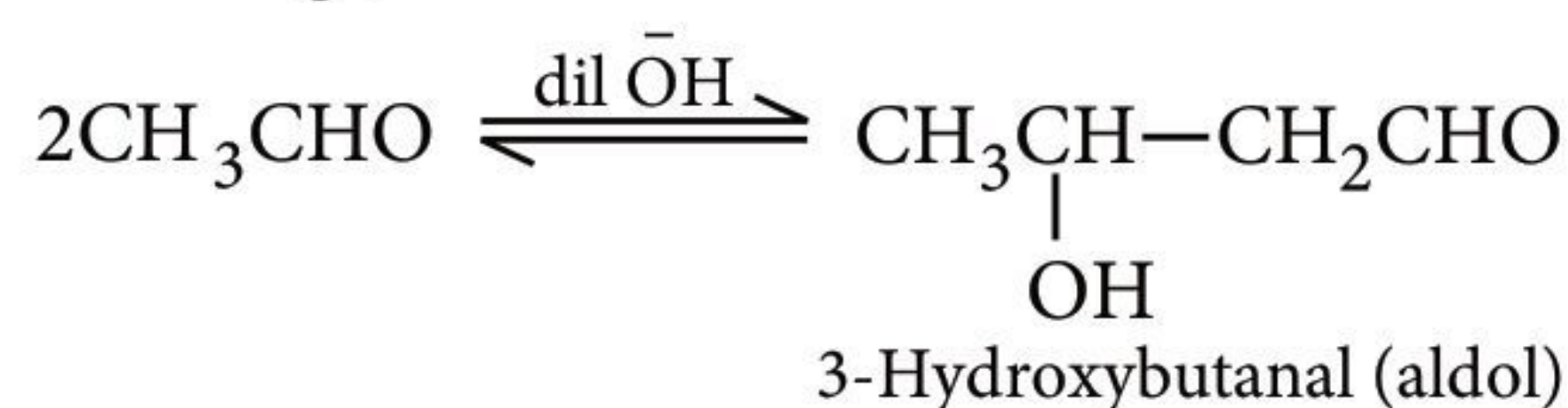


OR

(i) Aniline reacts with Hinsberg's reagent to form *N*-phenyl benzene sulphonamide which is soluble in KOH. On the other hand, *N*-methyl aniline reacts with Hinsberg's reagent to form *N*-phenyl-*N*-methyl benzene sulphonamide which is insoluble in KOH.



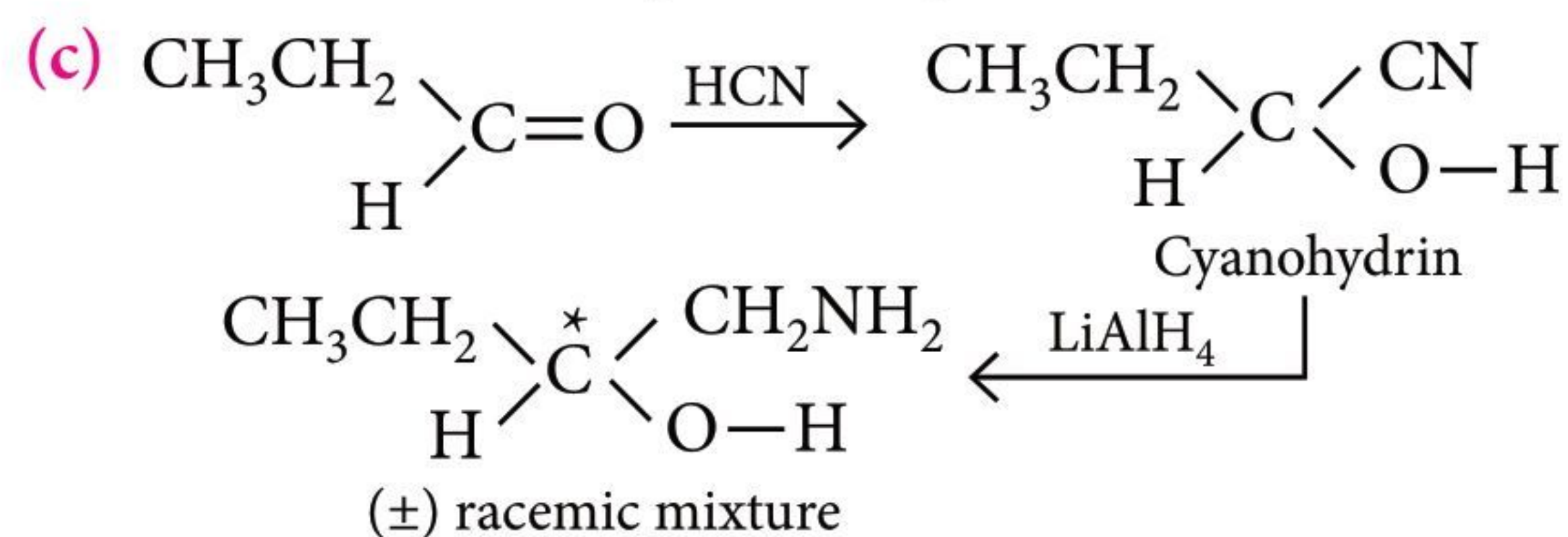
12. (a)  $\beta$ -Hydroxy aldehydes are called aldol. Aldehydes and ketones containing at least one  $\alpha$ -H atom undergo a reaction in the presence of dilute alkali to form aldol compounds. e.g.,



(b) Carbonyl group ( $>C=O$ ) polarises completely on demand of the reagent (electromeric effect) forming  $>\overset{+}{C}-\overset{-}{O}$  form, which when attacked by a nucleophile forms an intermediate anion  $>\overset{CN}{\underset{\substack{| \\ \cdot\cdot}}{C}}-\overset{-}{O}$  with negative

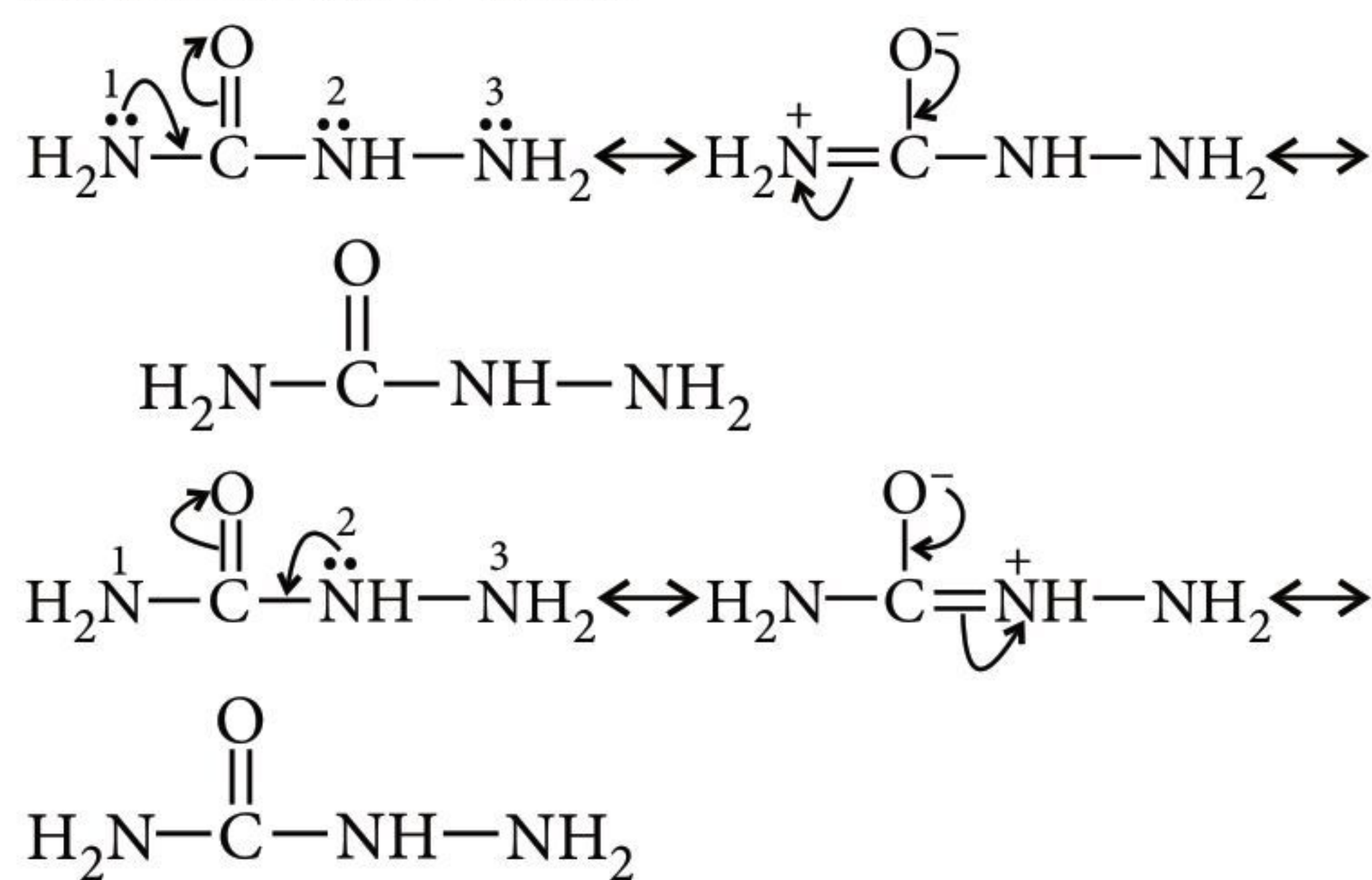
charge on more electronegative oxygen, hence stable. On the other hand, addition of a nucleophile to  $>C=C<$  (alkene) will result in the formation of an

anion  $>\overset{CN}{\underset{\substack{| \\ \cdot\cdot}}{C}}-\overset{-}{C}$  with carbon (not electronegative) carrying the negative charge, hence unstable and thus not reactive to nucleophilic reagents.



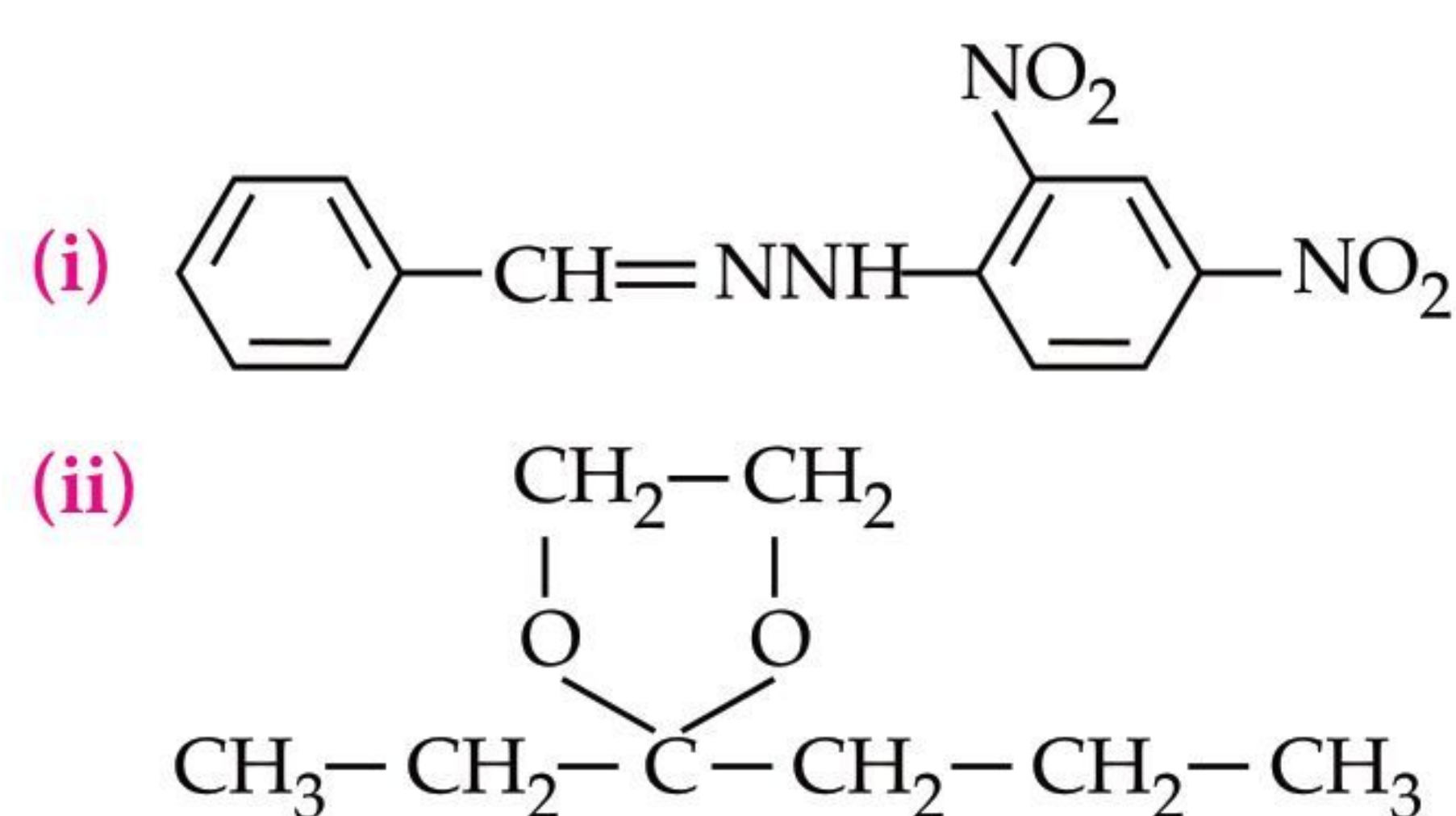
(d) (i) It is a nucleophilic addition reaction, in which  $CN^-$  acts as a nucleophile.  $CH_3CHO$  undergoes nucleophilic addition reactions faster than  $CH_3COCH_3$  as in  $CH_3COCH_3$  there are two electron releasing methyl groups attached to the carbonyl carbon that hinders the approach of nucleophile to carbonyl carbon and reduce the electrophilicity of the carbonyl group while in  $CH_3CHO$ , there is only one methyl group attached to carbonyl carbon.

(ii) Semicarbazide has the following resonating structures arising due to the electron withdrawing nature of the O atom.



Lone pairs of N-1 and N-2 are involved in conjugation with  $>C=O$  group while that of N-3 is not involved in resonance thus, it is involved in the formation of semicarbazone.

OR





**Total Marks : 120**

**Time Taken : 60 Min.**

### Only One Option Correct Type

- (a) the rate of desorption of adsorbed molecules from the surface does not depend on the surface covered
  - (b) the adsorption at a single site on the surface may involve multiple molecules at the same time
  - (c) the mass of gas striking a given area of surface is proportional to the pressure of the gas
  - (d) the mass of gas striking a given area of surface is independent of the pressure of the gas.
5. Equilibrium constant for the reaction in terms of  $\log K$  is  
$$2\text{Fe}^{3+} + 3\text{I}^- \rightleftharpoons 2\text{Fe}^{2+} + \text{I}_3^-$$
  
Given,  $\text{Fe}^{3+} + e^- \longrightarrow \text{Fe}^{2+}; E^\circ = 0.76 \text{ V}$   
$$\frac{1}{2}\text{I}_2 + e^- \longrightarrow \text{I}^-; E^\circ = 0.53 \text{ V}$$
  
(a) -3.89    (b) 3.98    (c) -7.78    (d) 7.78
6. The rate constant, the activation energy and the Arrhenius parameter of a chemical reaction at  $25^\circ\text{C}$  are  $3.0 \times 10^{-4} \text{ s}^{-1}$ ,  $104.4 \text{ kJ mol}^{-1}$  and  $6.0 \times 10^{14} \text{ s}^{-1}$  respectively. The value of the rate constant as  $T = \infty$  is  
(a)  $2.0 \times 10^{18} \text{ s}^{-1}$                   (b)  $6.0 \times 10^{14} \text{ s}^{-1}$   
(c) infinity                              (d)  $3.6 \times 10^{30} \text{ s}^{-1}$
7.  $\text{Pt(H}_2\text{)} \mid \text{pH} = 2 \parallel \text{pH} = 3 \mid \text{Pt(H}_2\text{)}$   
1 atm    1 atm  
The cell reaction for the given cell is  
(a) spontaneous                  (b) non-spontaneous  
(c) in equilibrium                (d) none of these.
8. The rate of a first order reaction is  $1.8 \times 10^{-3} \text{ mol L}^{-1} \text{ min}^{-1}$  when the initial concentration is  $0.3 \text{ mol L}^{-1}$ . The rate constant in the units of second is  
(a)  $1 \times 10^{-2} \text{ s}^{-1}$                   (b)  $1 \times 10^{-4} \text{ s}^{-1}$   
(c)  $6 \times 10^{-2} \text{ s}^{-1}$                   (d)  $6 \times 10^{-2} \text{ s}$ .



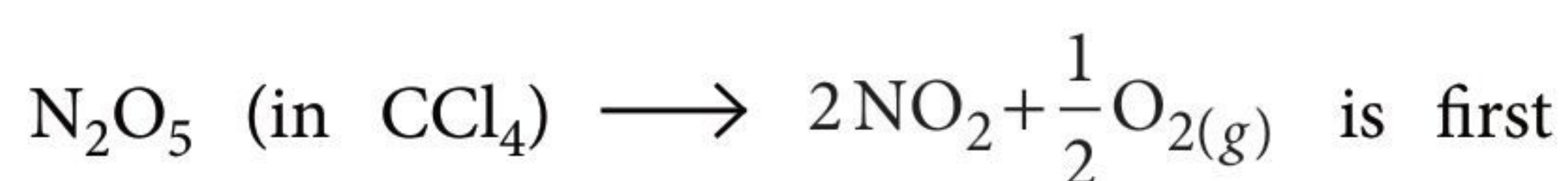
9. Which of the following electrolytes is least effective in causing coagulation of ferric hydroxide sol?

- (a) KBr (b)  $\text{K}_2\text{SO}_4$   
(c)  $\text{K}_2\text{CrO}_4$  (d)  $\text{K}_3[\text{Fe}(\text{CN})_6]$

10. In a galvanic cell, which one of the following statements is not correct?

- (a) Anode is negatively charged.  
(b) Cathode is positively charged.  
(c) Reduction takes place at the anode.  
(d) Reduction takes place at the cathode.

11. The reaction :



order with respect to  $\text{N}_2\text{O}_5$  with rate constant  $6.2 \times 10^{-4} \text{ s}^{-1}$ . What is the value of rate of reaction when  $[\text{N}_2\text{O}_5] = 1.25 \text{ mol L}^{-1}$ ?

- (a)  $7.75 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$   
(b)  $6.35 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$   
(c)  $5.15 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}$   
(d)  $3.85 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$

12. Amount of gas adsorbed per gram of adsorbent increases with pressure, but after certain limit is reached, adsorption becomes constant. It is where

- (a) multilayers are formed  
(b) desorption takes place  
(c) temperature is increased  
(d) all of the above.

#### Assertion & Reason Type

**Directions :** In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct choice as :

- (a) If both assertion and reason are true and reason is the correct explanation of assertion.  
(b) If both assertion and reason are true but reason is not the correct explanation of assertion.  
(c) If assertion is true but reason is false.  
(d) If both assertion and reason are false.

13. **Assertion :** The resistivity for a substance is its resistance when it is one meter long and its area of cross section is one square meter.

**Reason :** The SI units of resistivity are ohm metre ( $\Omega \text{ m}$ ) and ohm centimeter ( $\Omega \text{ cm}$ ).

14. **Assertion :** For arsenic sulphide sol,  $\text{BaCl}_2$  has lower coagulation value than  $\text{NaCl}$ .

**Reason :** Higher the valency of the oppositely charged ion of the electrolyte added, higher is the coagulating power of the electrolyte.

15. **Assertion :** For a second order reaction, graph of  $[\text{A}]$  vs.  $t$  is a straight line.

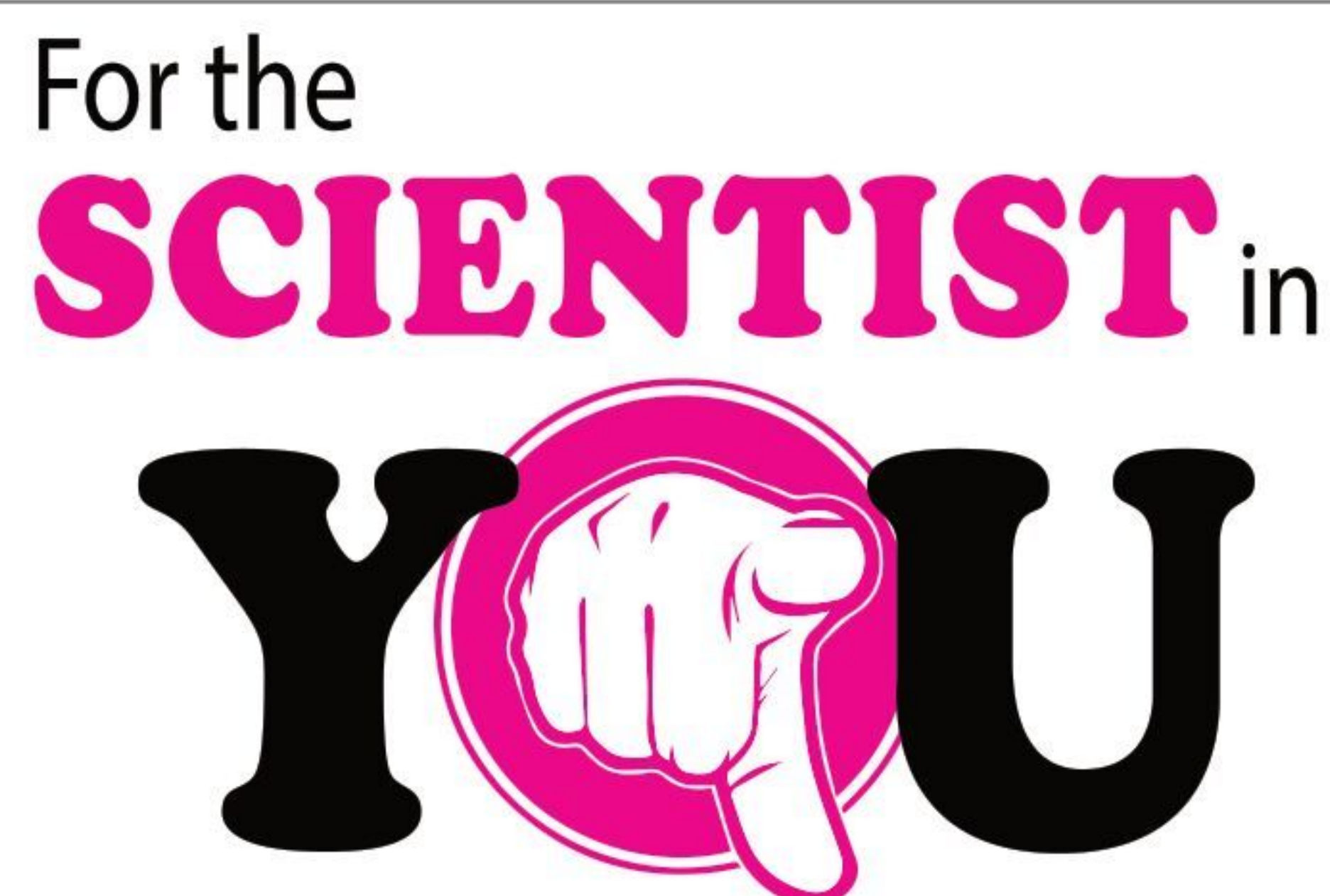
**Reason :** For second order reaction,  $[\text{A}] = kt + \frac{1}{[\text{A}]_0}$

#### JEE MAIN / JEE ADVANCED

#### Only One Option Correct Type

16. At  $380^\circ\text{C}$ , the half-life period for the first order decomposition of  $\text{H}_2\text{O}_2$  is 360 min. The energy of activation of the reaction is  $200 \text{ kJ mol}^{-1}$ . Calculate the time required for 75% decomposition at  $450^\circ\text{C}$ .

- (a) 41.12 min (b) 20.36 min  
(c) 10.18 min (d) 25.08 min



#### Scientists Design a Molecule with Great Potential for Treatment of COVID-19

A team of researchers have succeeded in designing a molecule that inhibits the replication of coronaviruses and has great potential for development into a drug, suitable for treating COVID-19. The molecule is effective against both the new variant and previously identified coronaviruses.

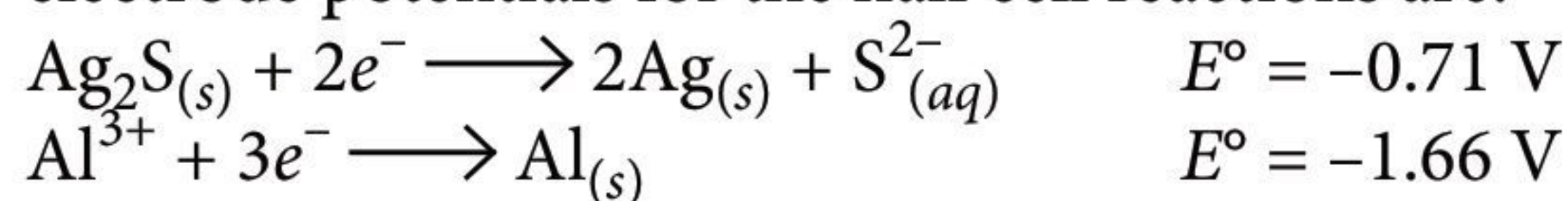
During the first month of the pandemic, researchers were able to determine the structure of the coronavirus and how it functions at the molecular level. One of the viral enzymes was identified as a promising target for a drug, which is a strategy that has been successful for other viral diseases, such as AIDS. The idea is to design a molecule with the ability to recognize and bind to the enzyme. This would block its activity and thereby prevent the virus from producing new virus particles, stopping the spread of the virus.

In 2020, researchers at Uppsala University, in collaboration with the Drug discovery and Development platform at Scilifelab, began to screen for inhibitors of the enzyme. They used computer models to identify molecules that can inhibit the enzyme's activity. This proved to be a faster way to discover starting points for the design of pharmaceuticals. Access to Swedish supercomputers has made it possible to evaluate several hundred million different molecules to find those that can bind to the enzyme. The molecules predicted by the models were then synthesized and tested in experiments.

"The most promising molecule shows the same ability to inhibit the replication of the new coronavirus as the active substance in Paxlovid, a combination drug recently approved for treating COVID-19. Our molecule works well on its own, and we have shown that the molecule is also effective against previously identified variants of the coronavirus," says associate professor and the article's lead author.

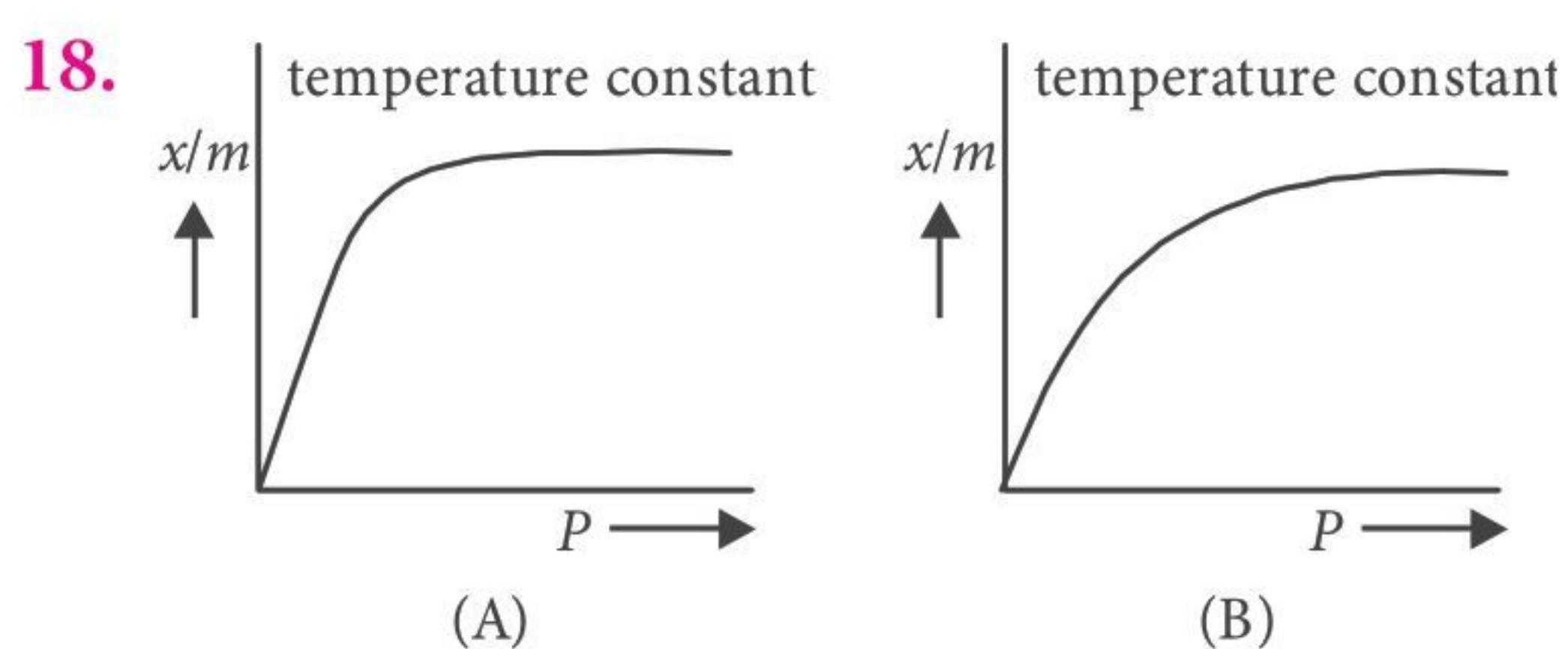


17. A tarnished silver article (tarnished silver contains  $\text{Ag}_2\text{S}$ ) was placed in an aluminium pan containing on inert electrolyte solution  $\text{NaCl}$ . The standard electrode potentials for the half cell reactions are:



Then,

- $E^\circ$  is negative for the reaction & tarnish will be removed
- $E^\circ$  is positive for the reaction & tarnish will not be removed
- $E^\circ$  is positive for the reaction & tarnish will be removed
- $E^\circ$  is negative for the reaction and tarnish will not be removed.

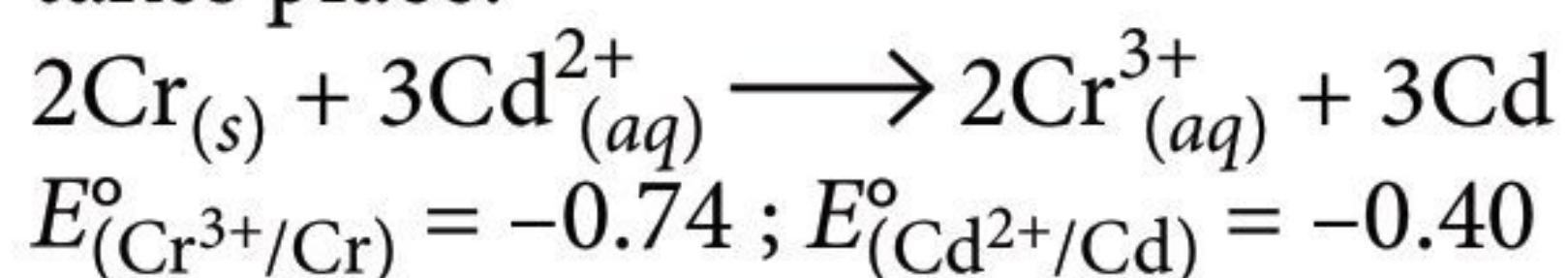


Which is correct statement?

- (A) represents Freundlich's adsorption isotherm while (B) represents Langmuir's adsorption isotherm.
  - (A) represents Langmuir's adsorption isotherm while (B) represents Freundlich's adsorption isotherm.
  - Both Freundlich and Langmuir adsorption isotherms have been found to be applicable in the adsorption of gases on solids only.
  - Change of pressure affects a lot and further adsorption can take place in both the isotherms.
19. 400 ml of standard gold sol is just prevented from coagulation by the addition of 0.96 g of starch before adding 1 ml of 10%  $\text{NaCl}$  solution, the gold number will be
- 2.4
  - 76
  - 240
  - 24

#### More than One Option Correct Type

20. For the galvanic cell in which following reaction takes place:



$$E^\circ_{(\text{Cr}^{3+}/\text{Cr})} = -0.74; E^\circ_{(\text{Cd}^{2+}/\text{Cd})} = -0.40$$

The correct statements are

- standard cell potential is +0.34 V
- standard cell potential is -0.34 V
- equilibrium constant for the reaction is  $3.76 \times 10^{34}$
- $\Delta G^\circ$  for the reaction is -159.57 kJ/mol.

21. What will happen during the electrolysis of aqueous solution of  $\text{CuSO}_4$  in the presence of Cu electrodes?

- Copper will deposit at cathode.
- Copper will dissolve at anode.
- Oxygen will be released at anode.
- Copper will deposit at anode.

22. Consider the following reaction for

$2\text{NO}_{2(g)} + \text{F}_{2(g)} \longrightarrow 2\text{NO}_2\text{F}_{(g)}$ . The expression for the rate of reaction in terms of the rate of change of partial pressures of reactant and product are

- $\text{rate} = -\frac{1}{2} \left[ \frac{dp(\text{NO}_2)}{dt} \right]$
- $\text{rate} = \frac{1}{2} \left[ \frac{dp(\text{NO}_2)}{dt} \right]$
- $\text{rate} = -\frac{1}{2} \left[ \frac{dp(\text{NO}_2\text{F})}{dt} \right]$
- $\text{rate} = \frac{1}{2} \left[ \frac{dp(\text{NO}_2\text{F})}{dt} \right]$

23. Which are not the examples of heterogeneous catalysis?

- Formation of  $\text{SO}_3$  in the chamber process
- Formation of  $\text{SO}_3$  in the contact process
- Hydrolysis of an ester in the presence of  $\text{H}^+$  ions
- Formation of vegetable ghee from vegetable oils

#### Integer / Numerical Value Type

24. 20% of surface sites of a catalyst are occupied by  $\text{N}_2$  molecules. The density of surface sites is  $6.023 \times 10^{14} \text{ cm}^{-2}$  and total surface area is  $1000 \text{ cm}^2$ . The catalyst is heated to 300 K while  $\text{N}_2$  is completely desorbed with a pressure of 0.001 atm and volume  $2.46 \text{ cm}^3$ . Then the active sites occupied by each  $\text{N}_2$  molecule is \_\_\_\_.
25. If it is desired to construct the following voltaic cell to have  $E_{\text{cell}} = 0.0860 \text{ V}$ . If  $[\text{Cl}^-]$  concentration that must be present in the cathodic half cell to achieve the desired emf is  $x \times 10^{-4}$ . Then value of  $x$  is \_\_\_\_.

## Quotable Quote

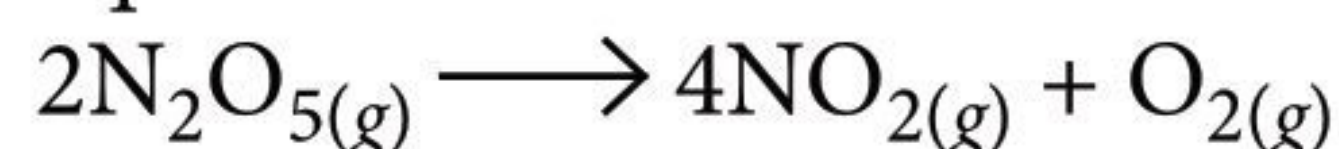
"The scientist is not a person who gives the right answers; he is one who asks the right questions."

**Claude Levi-Strauss**



$\text{Ag}_{(s)} | \text{Ag}^+ (\text{Sat. AgI}_{(aq.)}) || \text{Ag}^+ (\text{Sat. AgCl} \cdot x\text{MCl}^-) | \text{Ag}_{(s)}$   
(Given  $K_{sp}$  of AgCl and AgI are  $1.8 \times 10^{-10}$  and  $8.5 \times 10^{-17}$  respectively.)

26. Nitrogen pentoxide decomposes according to equation :



This first order reaction was allowed to proceed at  $40^\circ\text{C}$  and the data below were collected:

$[\text{N}_2\text{O}_5](M)$	Time (min)
0.400	0.00
0.289	20.00
0.209	40.00
0.151	60.0
0.109	80.0

The rate constant for reaction is  $x \times 10^{-2} \text{ min}^{-1}$ . Then  $x$  is \_\_\_\_\_.

### Comprehension Type

Order of reaction is an experimentally determined quantity. It may be zero, positive, negative and fractional. The kinetic energy equation of  $n^{\text{th}}$  order reaction is

$$k \times t = \frac{1}{(n-1)} \left[ \frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}} \right]$$

Half-life of  $n^{\text{th}}$  order reaction depends on initial concentration according to the following relation:

$$t_{1/2} \propto \frac{1}{a^{n-1}}$$

Unit of the rate constant varies with the order but general relation for unit of  $n^{\text{th}}$  order reaction is

$$\text{unit of } k = \left[ \frac{1}{\text{conc.}} \right]^{n-1} \times \text{time}^{-1}$$

The differential rate law for  $n^{\text{th}}$  order reaction may be given as :

$$\frac{dx}{dt} = k[A]^n$$

where  $A$  denotes the reactant.

27. In a chemical reaction  $A \rightarrow B$ , it is found that the rate of the reaction doubles when the concentration of  $A$  is increased four times. The order of the reaction with respect to  $A$  is  
(a) 0 (b)  $1/2$  (c) 1 (d) 2

28. The rate constant for zero order reaction is

(a)  $k = \frac{C_0}{2t}$  (b)  $k = \frac{C_0 - C_t}{t}$   
(c)  $k = \ln \frac{C_0 - C_t}{2t}$  (d)  $k = \frac{C_0}{C_t}$

29. Match column I with column II and select the correct answer using the code:

Column-I		Column-II	
A.	$\text{m}^{-1}$	p.	Molar conductivity
B.	$\text{S m}^2 \text{ mol}^{-1}$	q.	Conductance
C.	$\text{S m}^{-1}$	r.	Cell constant
D.	S	s.	Conductivity

A	B	C	D
(a) r	p	s	q
(b) p	q	r	s
(c) r	s	p	q
(d) p	r	s	q

30. Match column I with column II and select the correct answer using the code:

Column-I (Type of colloid)		Column-II (Example)	
A.	Liquid in solid	p.	Hair cream
B.	Gas in liquid	q.	Cheese
C.	Liquid in liquid	r.	Fog
D.	Liquid in gas	s.	Whipped cream

A	B	C	D
(a) q	p	r	s
(b) p	r	q	s
(c) q	s	p	r
(d) p	s	q	r



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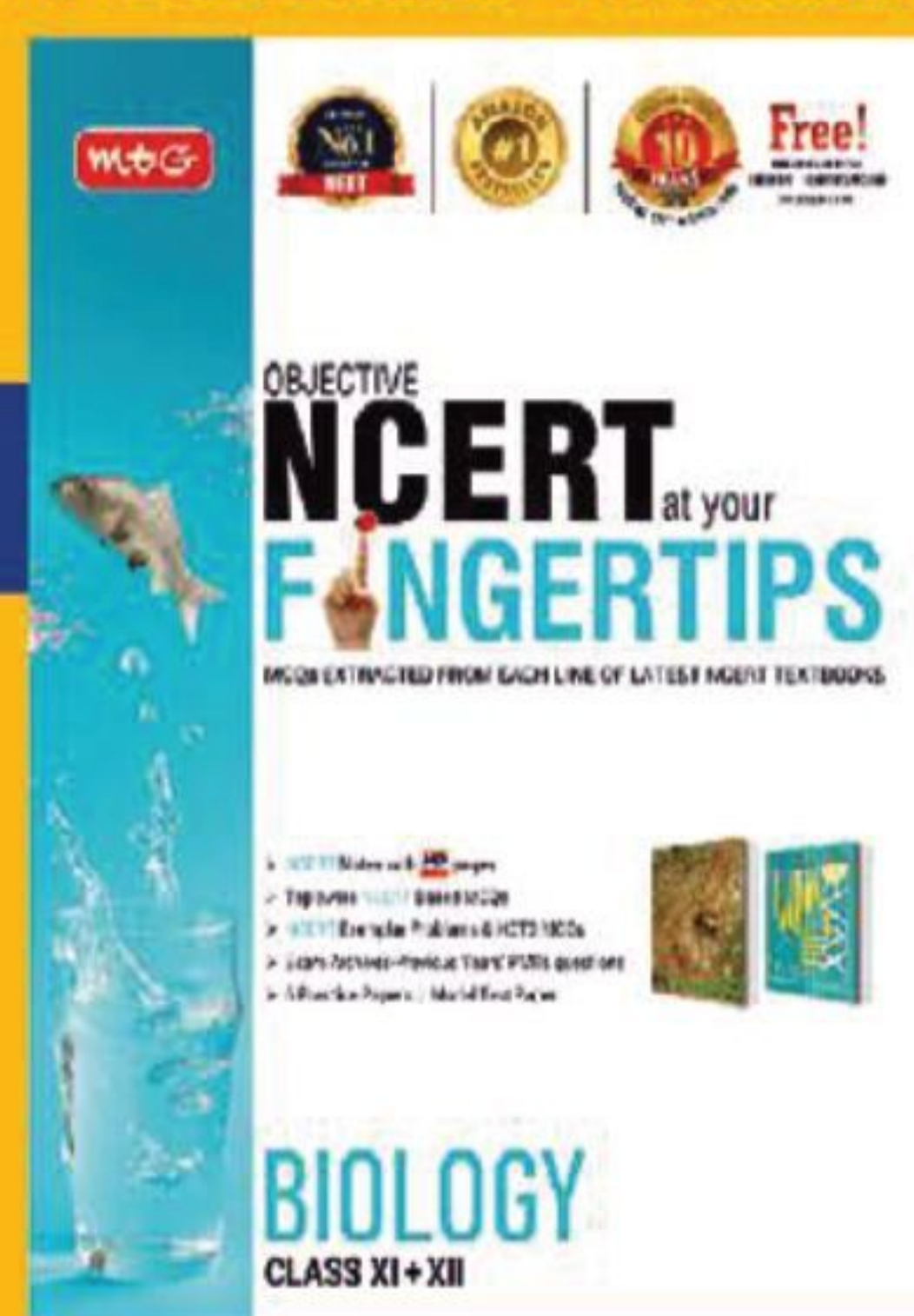
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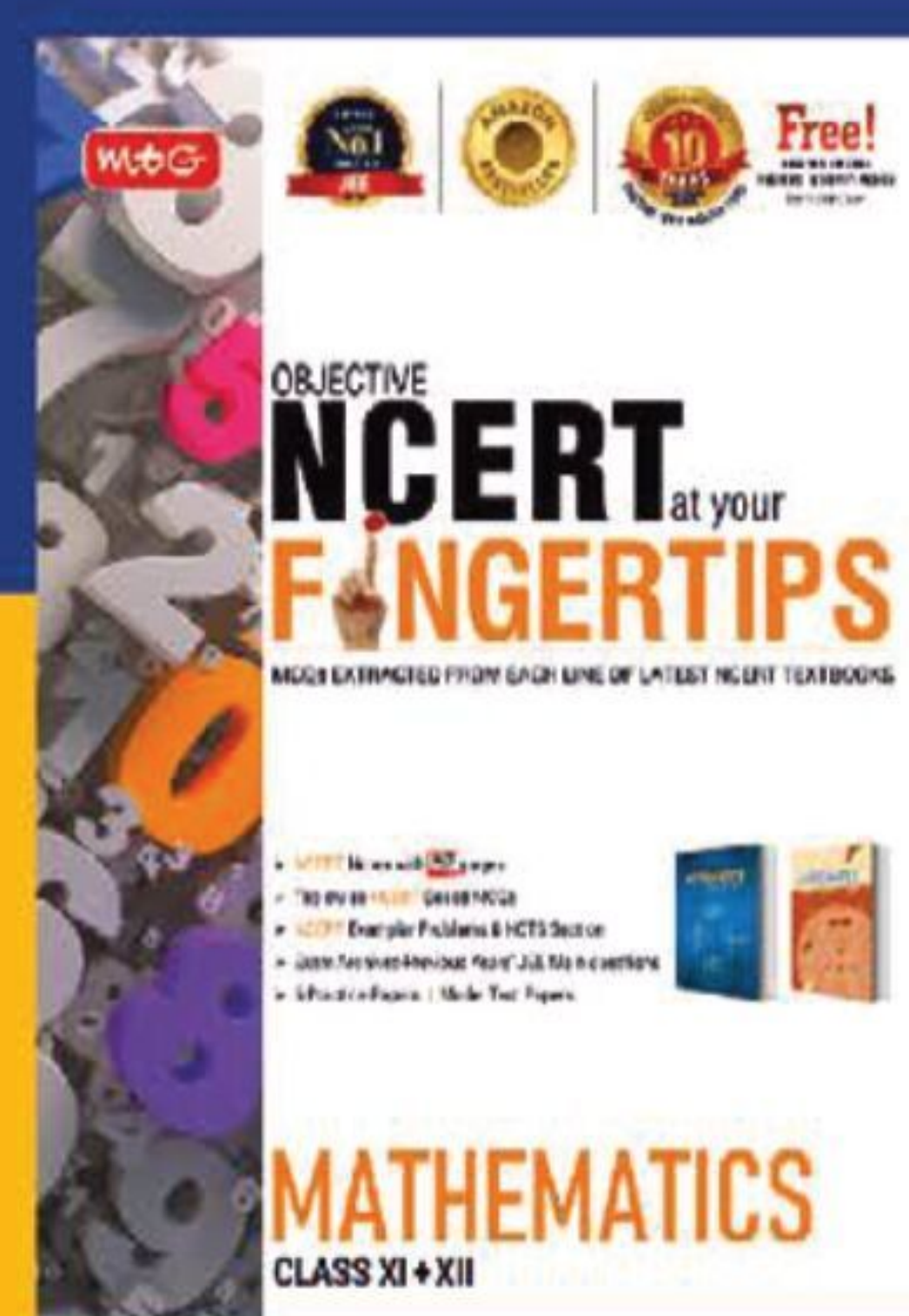
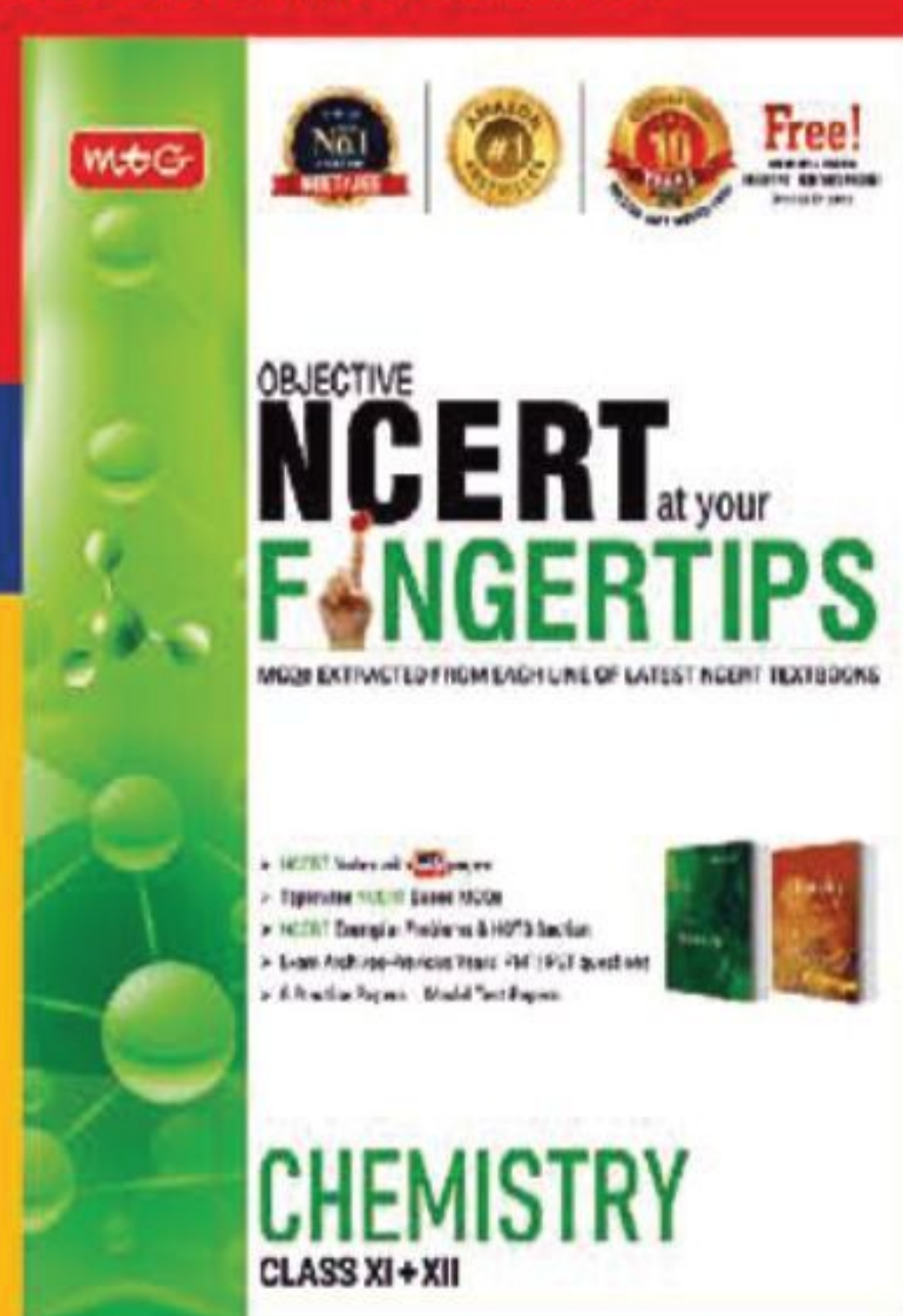
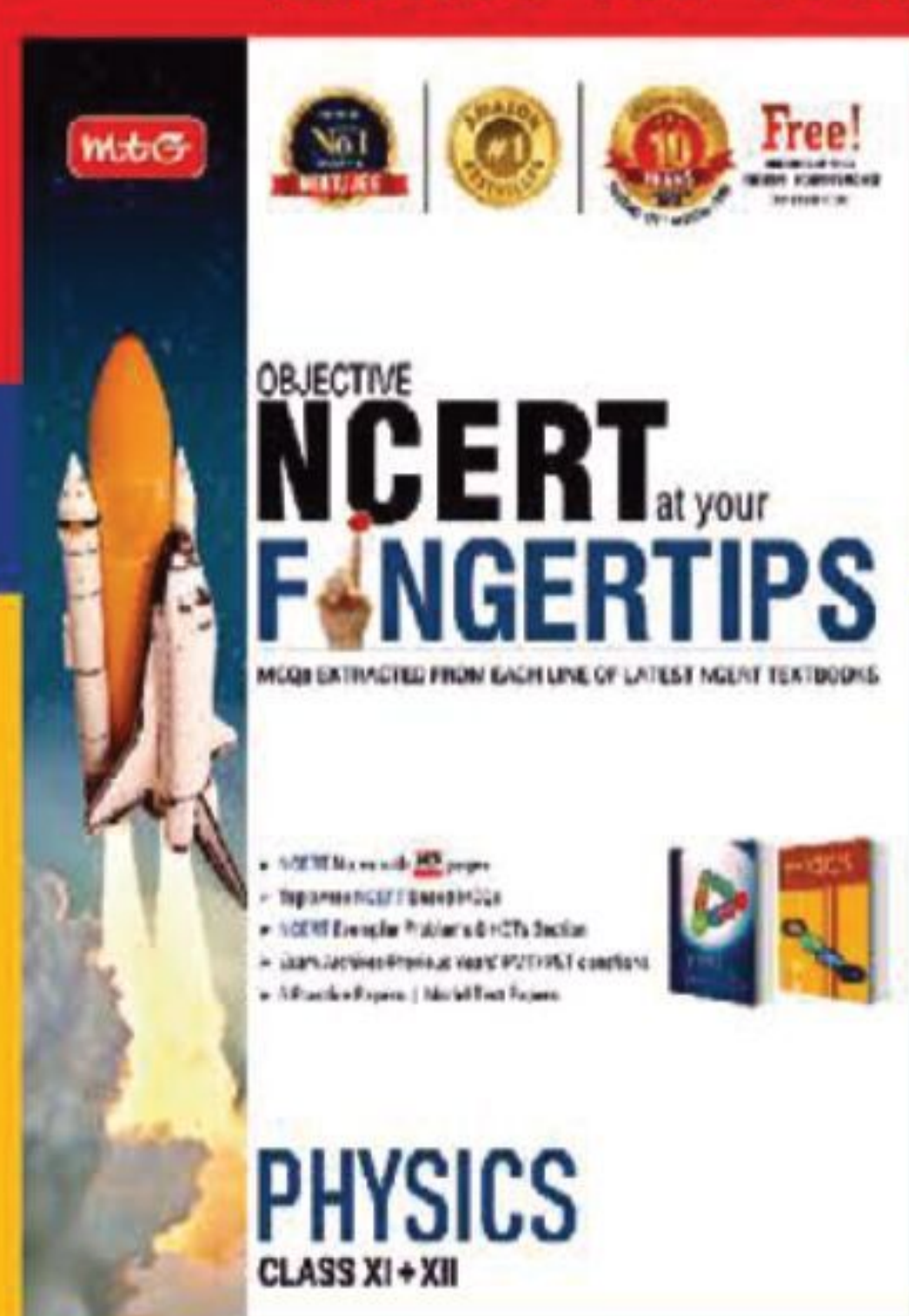
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